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NEW SYNTHETIC METHODS FOR SILICON-NITROGEN POLYMERS

L. W. Breed, J. C. Wiley, Jr., and R. L. Elliott
Midwest Research Institute

TECHNICAL REPORT AFML-TR-69-20, Part II

November 1970

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NEW SYNTHETIC METHODS FOR SILICON-NITROGEN POLYMERS

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FOREWORD

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under USAF Contract No. F33615-68-C-1371, "Research on New Synthetic Methods for Silicon-Nitrogen Polymers." The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg (LNP), as Project Scientist. Funds for this project are supplied to the Air Force Materials Laboratory by the Office of Aerospace Research.

This technical report covers the work conducted from 1 January to 31 December 1969.

The report was released by the authors in January 1970.

The work was carried out by Messrs. Richard L. Elliott, J. C. Wiley, Jr., and L. W. Breed, who acted as principal investigator.

This technical report has been reviewed and is approved.

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ABSTRACT

In condensation polymerizations of N,N'-bis[(dialkylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(p-hydroxydimethylsilylphenyl) ether, storage-stable, toluene-soluble polymers can be obtained provided the compositions are suitably stabilized with bis(trimethylsilyl)acetamide. If the dimethylamino derivative of the cyclodisilazane is used in the polymerization, polymers with inherent viscosities of about 0.3 dl/g are obtained; if the diethylamino derivative is used, polymers with inherent viscosities as high as 0.9 dl/g are produced. Other monomers examined in a preliminary way include the piperidino derivative of the cyclodisilazane and p-phenylenebis(methylvinylsilanol). Synthesis procedures are reported for p-phenylenebis(methylvinylsilanol), bis(p-hydroxydimethylsilylphenyl) ether, N,N'-bis [dimethyl(piperidino)silyl]tetramethylcyclodisilazane, 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane, 2,4,6-trimethyl-2,4,6-tris(-3,3,3-trifluoropropyl)cyclotrisilazane, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane, and various other intermediates and monomers. Several approaches are described for the preparation of phenyl-substituted cyclodisilazane monomers, and some additional investigations of equilibrium redistribution reactions are reported.

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I.

INTRODUCTION

The goal of this program is to develop new synthetic methods for high molecular weight silicon-nitrogen polymers. Approaches have been selected that afford the greatest probability of obtaining polymers with flexible backbones. The present report describes the results of research on this program conducted since the submission of AFML-TR-69-20, Part I, January 1969.

In earlier work, equilibrium redistribution of silicon-nitrogen and silicon-chlorine substances was employed to develop new methods of synthesis of monomers containing the cyclodisilazane and trisilylamine structures. Equilibrium redistribution was also employed to obtained oligomeric silazanes. A number of the chemical properties of the new monomers were investigated, particularly with respect to their usefulness in preparing polymeric compositions.

The most promising polymeric system proved to include the various polymers that can be prepared by condensing N,N'-bis[(dialkylamino)-dimethylsilyl]tetramethylcyclodisilazane with bis(p-hydroxydimethylsilylphenyl) ether. This report describes additional research on these polymers as well as new work on the synthesis of monomers and intermediates.

II.

DISCUSSION

A. Synthesis of Monomers, Intermediates, and Samples

1. Triethylsilylamine, tribenzylsilylamine, and triphenylsilylamine: Quantities of three silylamines were prepared: Triethylsilylamine, tribenzylsilylamine, and triphenylsilylamine. Attempts were made to obtain all three compounds in a high purity.

In the first attempt to prepare triethylsilylamine, triethylchlorosilane was added to a solution of ammonia in petroleum ether, but almost equal amounts of triethylsilylamine and hexaethyldisilazane were obtained as the product of the reaction. The hexaethyldisilazane was reconverted to chlorotriethylsilane with hydrogen chloride, then added to undiluted liquid ammonia. Under the latter conditions, aminotriethylsilane was the only product isolated from the product mixture. This observation is of somewhat general interest with respect to the preparation of silylamines. If the hexaethyldisilazane is formed by the condensation of two triethylsilylamine molecules, dilution would favor the formation of triethylsilylamine. But triethylsilylamine formation is favored in undiluted ammonia in which the mole ratio of ammonia to triethylsilylamine remains large, suggesting a competitive situation in which the added chlorotriethylsilane condenses directly with either triethylsilylamine or ammonia. The triethylsilylamine could be distilled at 137°* with no evidence of silazane formation.

Tribenzylsilylamine was prepared from "as received" chlorotribenzylsilane and ammonia in petroleum ether. When the tribenzylsilylamine was found to contain some tribenzylsilanol, apparently present in the starting material, the impure silylamine was reconverted to chlorotribenzylsilane with acetyl chloride and again treated with ammonia. In the second attempt, material with acceptable purity was obtained.

The "as received" chlorotriphenylsilane also contained some triphenylsilanol impurity. In one preparation the recrystallized chlorotriphenylsilane, from which the triphenylsilanol impurity had been removed, was used. In a second preparation triphenylsilanol impurities were removed by extracting the triphenylsilylamine from the triphenylsilanol with light petroleum ether. Samples were obtained whose total analyses for carbon, hydrogen, nitrogen, and silicon verified that no significant quantities of triphenylsilanol were present, but which showed the presence of a second impurity. The impurity, which was not identified, causes the triphenylsilylamine samples to have high analytical values for carbon and low values for nitrogen and silicon. The samples showed a single g.l.c. peak.

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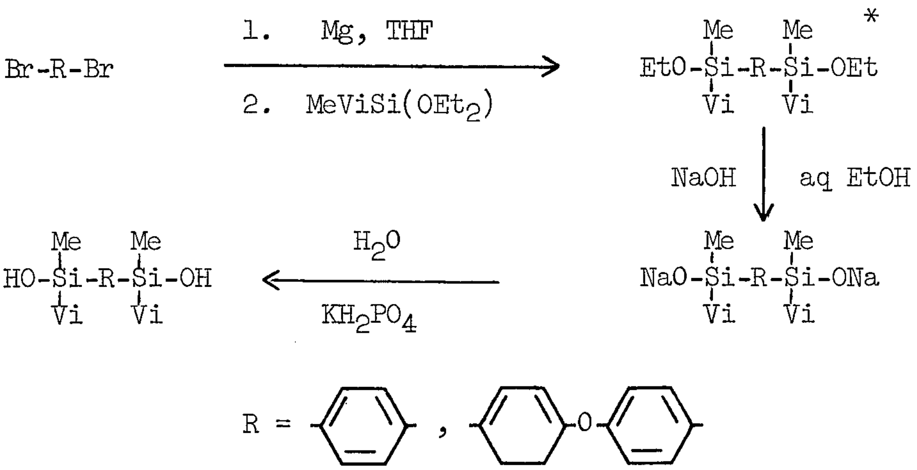
* All temperatures are reported in °C.

2. <u>Arylenedisilanols</u>: An additional 232-g. quantity of bis(<u>p</u>-hydroxydimethylsilylphenyl) ether was prepared by a method described earlier (AFML-TR-69-20) in an overall yield of 35% from bis(<u>p</u>-bromophenyl) ether. An older sample of the compound that had been stored for a year showed no signs of decomposition to the homopolymer.

The method of synthesis was satisfactorily extended to the preparation of <u>p</u>-phenylenebis(methylvinylsilanol) and bis(<u>p</u>-hydroxymethylvinylphenyl) ether.



The presence of the vinyl group resulted in little or no loss of yield in the syntheses. Both intermediate ethoxy derivatives were separated, purified, and characterized. In addition, <u>p</u>-phenylenebis(methylvinylsilanol) has also been purified and characterized by elemental analyses. The disilanol derived from phenyl ether has been characterized by infrared and n.m.r. spectral analysis, but difficulties have been encountered in effecting the necessary purification through crystallization. These vinyl derivatives were prepared to provide crosslinking sites in polymeric compositions.

3. <u>Cyclodisilazane derivatives</u>: The synthesis of cyclodisilazane derivatives during this report period has been largely limited to the repetition of procedures described in previous reports for monomers needed for arylenedisilanol condensation polymerizations or their intermediates. The substances prepared include N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane, and N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane. A new monomer, N,N'-bis[dimethyl(piperidino)]tetramethylcyclodisilazane was prepared by treating N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane with the lithium salt of piperidine.

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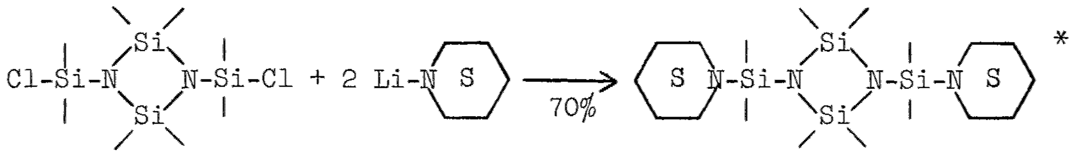
* Throughout the report, Ph = -C_6H_5, Me = -CH_3, and Vi = -CH = CH_2.



A repetition of the preparation of N,N'-bis(anilinodimethylsilyl)-tetramethylcyclodisilazane from the monolithium salt of aniline rather than the free base increased the proportion of the product that could be recovered to 65%. An attempt to effect a condensation between dimethylphenylsilanol with N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane in the presence of sodium hydride, which is a method analogous to an earlier used polymerization procedure, failed to given any N,N'-bis[dimethyl(dimethylphenylsiloxy)silyl]tetramethylcyclodisilazane. At least half of the weight of the starting materials was recovered as lower-boiling products.

Some work was completed on attempts to prepare the phenyl-substituted cyclodisilazane derivative, N,N'-bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane. It was recently reported that when dichlorodiphenylsilane and N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane were heated to about 300°, transsilylation occurred with the formation of dichlorodimethylsilane and phenyl-substituted cyclodisilazane derivatives (Ref. 1). In an attempt to modify this procedure and use dichloromethylphenylsilane in place of dichlorodiphenylsilane, the temperature to which the mixture could be heated was limited by the presence of dichloromethylphenylsilane. Some dichlorodimethylsilane distilled, but the boiling temperature of the mixture only increased from 200-210°. After the product was treated with dimethylamine, 63% of the dichloromethylphenylsilane could be recovered as its dimethylamine derivative, but only about 15% of the cyclodisilazane with no phenyl substitution was separated. The remainder of the product was of a rather indefinite structure, but did contain phenyl substitution according to infrared analysis.

An alternate approach for preparing N,N'-bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane was also attempted. The method followed was analogous to the procedure employed by Rochow for preparing N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane from 1,3-dichlorotetramethyldisilazane and sodium bis(trimethylsilyl)amide (Ref. 2). 1,3-Dichloro-1,3-diphenyl-1,3-dimethyldisilazane was treated with sodium bis-(trimethylsilyl)amide, but the product was not N,N'-bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane. When the condensate was treated with dimethylamine, the n.m.r. spectrum of the derivative did not indicate the presence of dimethylamine groups and the infrared spectrum did not have characteristic absorptions of the cyclodisilazane ring. The infrared spectrum, the n.m.r. spectrum and the elemental analysis were consistent with the product being 1,3-bis[bis(trimethylsilyl)amino]-1,3-dimethyl-1,3-diphenyldisilazane.

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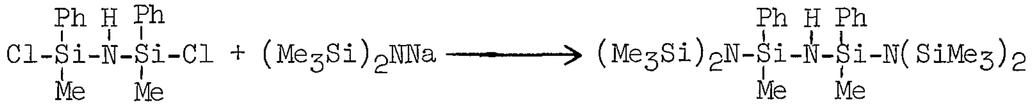
* Throughout the report all unfilled valences indicate methyl groups.



$$Cl-\overset{Ph}{\underset{Me}{Si}}-\overset{H}{N}-\overset{Ph}{\underset{Me}{Si}}-Cl + (Me_3Si)_2NNa \longrightarrow (Me_3Si)_2N-\overset{Ph}{\underset{Me}{Si}}-\overset{H}{N}-\overset{Ph}{\underset{Me}{Si}}-N(SiMe_3)_2$$

The failure to obtain the cyclodisilazane under these conditions eliminates the procedure as a method of obtaining phenyl-substituted cyclodisilazanes.

4. <u>Trisilylamine derivatives</u>: Because the diethylamino group in cyclodisilazanes proved to be a better leaving group in condensation polymerizations with arylenedisilanols, attempts were made to prepare bis[(diethylamino)dimethylsilyl]trimethylsilylamine so that the trisilylamine group could be incorporated, in polymeric compositions. All attempts, either by treating bis(chlorodimethylsilyl)trimethylsilylamine with diethylamine or its lithium salt, failed to produce an identifiable product. N.m.r. spectral data on products that were isolated indicated that only one of the chlorine atoms in the substituted trisilylamine was being replaced in the condensation.

In a parallel experiment, 1,3-dichlorotetramethyldisilazane was treated with diethylamine and no difficulty was encountered in separating 1,3-bis(diethylamino)tetramethyldisilazane. This difference in reactivities again suggests that, in the trisilylamine structure, conformational restraints imposed when the N-H in a disilazane is replaced by N-$SiMe_3$ effects steric limitations on the extent to which the compounds can undergo substitution reactions.

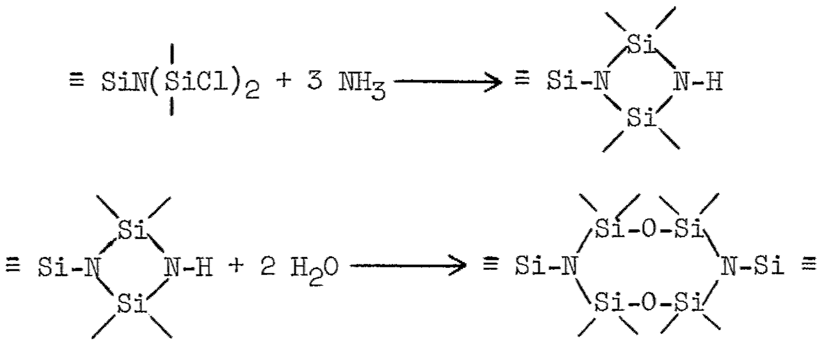
Some consideration was also given to the intermediate, N-sodiohexamethylcyclotrisilazane. This substance would be useful in the preparation of trisilylamine intermediates in the manner that has been described in earlier reports. However, the reagent previously used for its preparation, the sodium-styrene radical anion, caused the formation of by-products such as diphenylbutane, which were difficult to separate from the trisilylamines.

As a first approach it was intended to prepare the salt with the usual sodium-styrene adduct, separate the solid material and wash away the by-products with organic solvents. In this way, a 49% yield of the salt was obtained, but it could not be characterized by elemental analysis. It was characterized by converting it to N-trimethylsilylhexamethylcyclotrisilazane with chlorotrimethylsilane in a 46% yield. Alternately, a sodium salt was obtained (67%) by treating hexamethylcyclotrisilazane with sodium amide by the procedure usually employed for the preparation of sodium bis(trimethylsilyl)amide (Ref. 3) from hexamethyldisilazane. This salt was also characterized by its conversion (20%) to N-trimethylsilylhexamethylcyclotrisilazane.

Both methods gave a solid sodium salt that could be converted to the trimethylsilyl derivatives, but the overall conversion by neither procedure was high. Still, these procedures provide a method by which pure phenyl-substituted trisilylamines could be prepared.

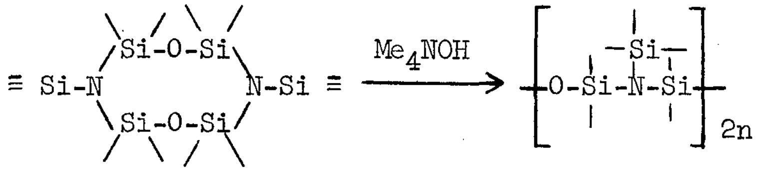
It was also found that N-trimethylsilylhexamethylcyclotrisilazane condenses with sodium amide to give a crystalline product that does not contain cyclodisilazane groups. The characterization of this product is incomplete.

An unsuccessful attempt to prepare 1,5-bis(trimethylsilyl)-1,5-diaza-3,7-dioxa-2,4,6-tetrasilaoctamethylcyclooctane by treating bis(chlorodimethylsilyl)trimethylsilylamine and sodium oxide was reported in AFML-TR-66-116 (Part III), p. 24. The synthesis of this compound was attempted because of the possibility that it might undergo a base-catalyzed linearization to give a polymer containing the trisilylamine structure. A recent publication (Ref. 4) reported that the compound could be prepared by the heterogeneous hydrolysis of 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane, which in turn could be prepared from bis(chlorodimethylsilyl)-trimethylsilylamine and ammonia.



These procedures were repeated. An earlier attempt to prepare 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (AFML-TR-66-116, Part II, p. 47) had failed because the ammonolysis product had not been distilled away from the soluble ammonium salts at low temperature before it was fractionally distilled. This precaution was found necessary in later work on 1-methyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane. This necessary precaution is not pointed out in the recent report of its preparation (Ref. 4). An attempt to obtain the siloxazane monomer by heterogeneous hydrolysis of 1-methyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane was unsuccessful.

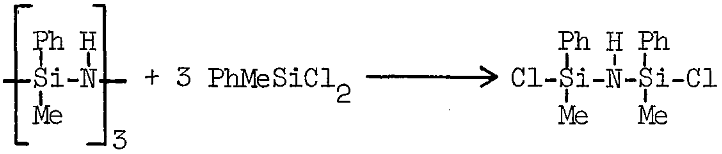
When 1,5-bis(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane was stirred at room temperature with 1 wt % of tetramethylammonium hydroxide, a soft gum formed within 7 min.



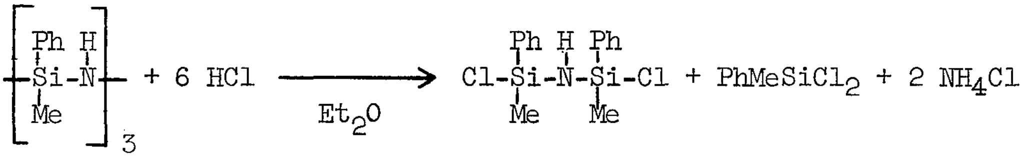
Although the inherent viscosity of the product was low, the system merits further investigation.

5. <u>2,4,6-Trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane, and 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane</u>: 2,4,6-Trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane and 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane were prepared for future use in equilibration reactions to obtain substituted cyclodisilazane monomers. Both substances were readily obtained by treating the appropriate chlorosilanes with ammonia under the usual conditions. Although the 3,3,3-trifluoropropyl derivative is reported to melt at 74-82° (Ref. 5), the material obtained in this work melted at 41-45°, but its identity was confirmed by elemental analyses. Both substances could be readily purified by distillation.

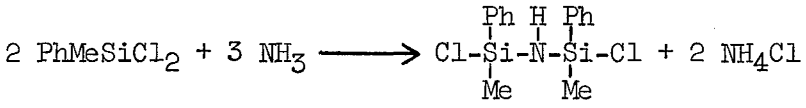
1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisilazane was prepared as an intermediate in attempts to obtain phenyl-substituted cyclodisilazanes through condensation with sodium bis(trimethylsilyl)amide. Initially, three procedures were attempted for its preparation, each of which provided only a low conversion.



$$\left[-\overset{Ph}{\underset{Me}{Si}}-\overset{H}{N}-\right]_3 + 3\ PhMeSiCl_2 \longrightarrow Cl-\overset{Ph}{\underset{Me}{Si}}-\overset{H}{N}-\overset{Ph}{\underset{Me}{Si}}-Cl$$



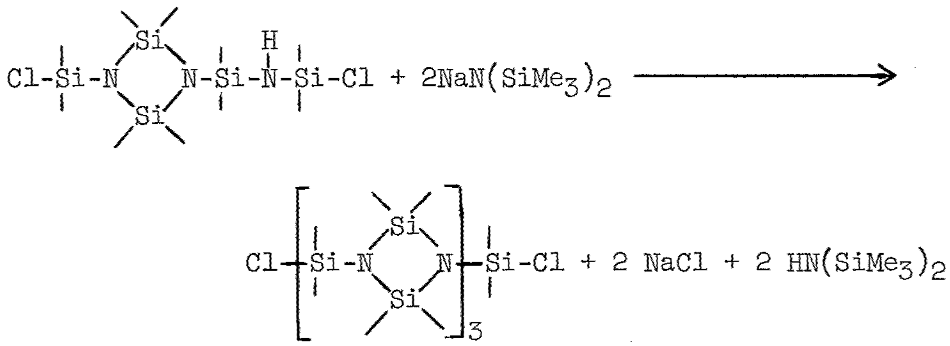
$$\left[-\overset{Ph}{\underset{Me}{Si}}-\overset{H}{N}-\right]_3 + 6\ HCl \xrightarrow[Et_2O]{} Cl-\overset{Ph}{\underset{Me}{Si}}-\overset{H}{N}-\overset{Ph}{\underset{Me}{Si}}-Cl + PhMeSiCl_2 + 2\ NH_4Cl$$



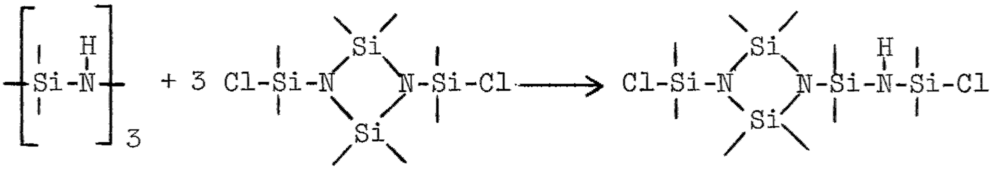
$$2\ PhMeSiCl_2 + 3\ NH_3 \longrightarrow Cl-\overset{Ph}{\underset{Me}{Si}}-\overset{H}{N}-\overset{Ph}{\underset{Me}{Si}}-Cl + 2\ NH_4Cl$$

A satisfactory conversion was obtained, however, when the mole ratio in the equilibration between dichloromethylphenylsilane and 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane was increased from 3:1 to 4:1. Even under these conditions the yield was only 33% suggesting that even a higher mole ratio might be preferred.

6. Equilibration reactions: If oligomerization of cyclodisilazanes can occur through the dimerization of N-chlorodimethylsilyl-N'-(3-chlorotetramethyldisilazanyl)tetramethylcyclodisilazane , the method could provide a procedure for the high yield preparation of the oligocyclodisilazane with three rings, provided the intermediate could be isolated in sufficient quantities.



The synthesis of the intermediate was investigated by equilibrating 3:1 mole ratios of hexamethylcyclotrisilazane and N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, distilling the product, and determining the product composition by g.l.c.



Because the highest conversion to the disilazanyl derivative in this equilibration was 15-20%, the approach has been abandoned.

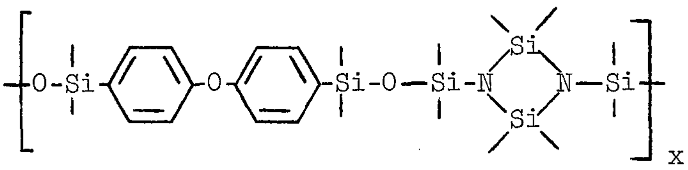
The possibility that N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane could disproportionate to give oligocyclodisilazanes was also considered. However, when the compound was heated for an extended period at its normal boiling point, the reflux temperature of the mixture did not change.

When aluminum chloride and N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane were heated under various conditions, substantial proportions of nonvolatile, toluene-soluble residues were obtained in some of the experiments. The products were apparently not oligocyclodisilazanes.

Several other equilibration reactions were completed. In one a variation in the procedure did not greatly change the conversion to N,N'-bis-(chlorodimethylsilyl)tetramethylcyclodisilazane. A second equilibration was carried out at a higher temperature and quenched with diethylamine. The diethylamine derivatives of the oligocyclodisilazanes were found to be even more difficult to separate than the dimethylamine derivatives.

B. Polymer Preparation and Properties

In work at the Air Force Materials Laboratory, Wright-Patterson Air Force Base, condensates of N,N'-[bis(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(p-dimethylhydroxysilylphenyl) ether with inherent viscosities in the range of 0.2 dl/g have been milled with filler and found to have desirable properties as elastomers. One problem that prevented the further development of these elastomers was that the gums obtained in the condensation polymerization underwent a crosslinking reaction on storage at room temperature in several days and became rubbery and nonmillable. Considerable work during the period covered by this report has concerned this polymerization reaction particularly with respect to finding a reliable procedure for obtaining higher molecular weight, stable polymers that can be milled. The polymer structure can be represented as follows:



1. N,N'-[Bis(dimethylamino)dimethylsilyl] tetramethylcyclodisilazane-bis(p-hydroxydimethylsilylphenyl) ether condensates: Initially some work was done to determine qualitatively the range of polymer consistencies that would allow the polymer to be mixed with a filler and curing agent. In order to obtain a range of consistencies, a number of polymer samples were prepared at different temperatures--60°, 90°, 120°, and 150°--from both the diethylamino- and the dimethylamino-derivative of the cyclodisilazane. The repeatability in this series was poor, but it became clear that only a gum consistency was satisfactory for milling. Rubbery unmillable samples were obtained in at least one experiment at all temperatures above 60°, and one of the 60° samples became nonmillable after five days.

In another series of experiments, various mixing conditions were examined in a procedure in which the monomers were mixed in toluene, the toluene was evaporated, and the mixing was continued at room temperature. The variations in the procedure did not appear to significantly affect the nature of the polymer that was obtained. Although most of these polymers were not completely soluble in toluene, they remained millable for over a month.

Solution polymerization was also reinvestigated. Earlier it had been found that gelation occurred when the monomers were heated in toluene solution so that most of the preliminary work had employed bulk polymerizations. When further work was carried out on solution polymerization, gelation occurred in less than an hour when 0.0025 mole of the monomers was heated in 5 ml. of toluene. However, when the dilution was increased to 10 and 20 ml., the mixtures could be heated at least 7 hr. without gelation. Removal of the solvent under reduced pressure gave gums with inherent viscosities of about 0.15 dl/g.

The most significant observations that have been made at this point in the experimental work was that when some of the low molecular weight gums were treated with bis(trimethylsilyl)acetamide in toluene solution and the mixtures were refluxed, gums with inherent viscosities of about 0.2 dl/g were obtained. When two samples from the same polymerization, one treated with bis(trimethylsilyl)acetamide and the other not treated, were heated at 150°, the treated sample remained toluene-soluble and the untreated sample gelled quickly. The gum treated with bis(trimethylsilyl)-acetamide could be dissolved in toluene and washed with water to remove the acetamide impurity and recovered unchanged. Its inherent viscosity after the water treatment was 0.19 dl/g.

But even with a procedural modification involving solution condensation and the use of an endcapping agent, results of polymerizations continued to be erratic. Seemingly identical conditions gave gelation in some experiments and soluble polymers with considerably different molecular weights in others. Subsequently, it was observed that when heating mantles were used, even in the solution condensation step, some gelation could be detected near the walls of the polymerization flask. Therefore, the use of mantles, which could cause local overheating, was abandoned and steam baths and Wood's metal baths were used in the various heating steps. With this change, erratic gelation of polymerization batches was nearly eliminated.

It remained important, however, to be able to predict that a polymer would not increase in viscosity on storage. Since polymers that did not gel when they were heated at 150° for 2 hr. also did not show significant increases in viscosity on prolonged storage, this heating step was selected as a criterion for storage stability.

Once the problem of localized overheating with the heating mantles had been eliminated, scale-up experiments were undertaken. At three of the four molar levels employed, repeatability in the results of the final solution viscosity of the polymers was good; however, in one experiment an abnormally high viscosity was obtained, indicating that procedural variables had not been entirely eliminated. These experiments did indicate that under the conditions of the polymerization, inherent viscosities of about 0.3 dl/g could be expected.

2. *N,N'-[Bis(diethylamino)dimethylsilyl]tetramethylcyclodisilazane-bis(p-hydroxydimethylsilylphenyl) ether condensates:* Since the polymers from N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane seemed to be limited to inherent viscosities of about 0.3 dl/g when conditions were adopted that would insure freedom from gelation, a series of experiments was undertaken with N,N'-bis(diethylaminodimethylsilyl)tetramethylcyclodisilazane. Diethylamine, which has a larger K_B than dimethylamine, should be a better leaving group in the condensation with bis(*p*-dimethylhydroxysilylphenyl) ether; therefore, if the ring silazane group competes with the pendant silylamine group in the polymerization, reaction at the pendant group would be more highly favored in the diethylamine derivative.

In the first experiments with these monomers, the effect of the concentration level of bis(trimethylsilyl)acetamide endcapping agent in the procedure was investigated. As a step in the method, the polymers were heated at 150° for 2 hr., a procedure that had caused gelation of the polymers derived from the dimethylamine derivative when insufficient bis(trimethylsilyl)acetamide had been used. None of these polymers gelled; therefore, the bis(trimethylsilyl)acetamide level was selected that gave the highest inherent viscosity. The high and low levels gave lower inherent viscosities. A number of experiments were carried out at the selected level, but the choice ultimately proved to be incorrect, and a higher level was needed to stabilize the polymer. This fact became evident when viscosity increases were observed in samples over long periods of storage and when a larger sample lost its solubility after a relatively short storage period.

A treatment of 200° for 2 hr., however, gave results that correlated with the level of endcapping agent and the storage stability of the polymers. Polymers which had low levels of bis(trimethylsilyl)acetamide gelled under these conditions. One of them had shown a considerable increase in inherent viscosity after a month's storage. Polymers that were prepared with higher levels of bis(trimethylsilyl)acetamide did not gel and did not change significantly in inherent viscosity after a month's storage. It therefore appeared that the 200° heating could be used to screen the polymers. This conclusion was confirmed in a larger scale polymer, which was presumed to be storage stable because it did not gel at 150°, but which did gel at 200° and was later found to crosslink after a moderately short storage period.

Several other features of this polymerization merit comment. It is evident that the inherent viscosities of the systems continue to increase in many of the experiments throughout the various steps. In general, this tendency is greater with lower levels of endcapping reagent and reflects the fact that a portion of the free silanol groups may remain after the endcapping step and that these groups may continue to advance the polymerization. In this connection, the very low inherent viscosities obtained at the end of the solution polymerization step indicate that the condensation product is little more than a prepolymer and that the building of polymer chain length occurs during the heating steps. The treatment with bis(trimethylsilyl)acetamide is probably not truly an encapping step, but one in which a portion of the residual silanol functionality is blocked.

In order to better control the polymerization a number of the polymer preparations were heated for a period immediately following the solution polymerization step but preceding the endcapping step. Even with the advancement of the polymerization at this stage, additional polymerization occurred after the endcapping step. One polymer which was heated at 150°, suffered solubility loss before the completion of the experiment. These results verify the conclusion that although gelation can be avoided through the use of the endcapping reagent, not all possible sites for the advancement of the polymerization are removed.

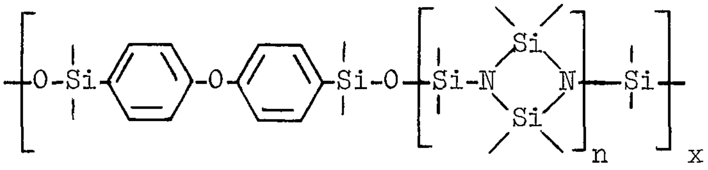
Subsequently, five condensates of N,N'-bis(diethylaminodimethylsilyl)-tetramethylcyclodisilazane and bis(p-dimethylhydroxysilylphenyl) ether were prepared on a 0.02 mole scale to obtain samples. In three of these experiments, reasonably good replication of results was obtained--the condensates had inherent viscosities of 0.88, 0.69, and 0.60 dl/g, respectively. In the two other experiments, however, materials with much lower inherent viscosities were obtained. The results of one of those experiments could be accounted for on the basis of one sample of the cyclodisilazane monomer not having been sufficiently pure. The infrared spectra of the low viscosity polymers did not differ significantly from the spectra of the higher molecular weight materials.

In another series of polymerizations at the 0.07 molar level, the final condensate had an inherent viscosity of 0.89 dl/g. Portions of this polymer sample, however, were further heated before the endcapping step to advance the polymerization, and although the samples did not crosslink during the heating step, they very rapidly lost their solubility after the heat treatment was complete.

One polymerization was carried out to determine the effectiveness of dimethylphenylsilanol as an endcapping agent, but the silanol did not prevent the ultimate loss of solubility in the polymer. A product from a parallel experiment that was endcapped with bis(trimethylsilyl)acetamide had an inherent viscosity of 1.11 dl/g, which is probably the highest viscosity obtained with this system.

3. Hydrolytic and thermal stabilities of N,N'-bis[(dialkylamino)-dimethylsilyl]tetramethylcyclodisilazane - bis(p-hydroxydimethylsilylphenyl) ether condensates: A method which was devised for comparing the hydrolytic stabilities of various silicon-nitrogen polymers was first used to examine several polymers that had not been treated with bis(trimethylsilyl)acetamide. Polymer films were cast on a KRS-5 optic, exposed to moist air, and infrared spectra of the polymers were determined at specified time intervals. Hydrolysis rates could be followed by determining the initial intensities of the $SiCH_3$ band at 1255 cm^{-1} for each polymer and the intensity of the cyclodisilazane band at 1035 cm^{-1} at each time interval.

In order to compare the hydrolytic stability of various silazane structures, polymers based on the following compositions were prepared:



where n = 1, 2, and 4.

The results of the hydrolytic stability studies are reported in Figure 1*. The slopes of the curves in the 10-50-hr. range are indicative of the relative hydrolytic stabilities and show that the oligocyclodisilazane polymers are more hydrolytically stable than the polymers containing single cyclodisilazane rings, but that all the polymers do undergo some hydrolytic degradation under these conditions.

The hydrolysis rate of an endcapped polymer (η_{inh} = 0.26 dl/g) was much slower than the rate for a nonendcapped polymer (η_{inh} = 0.22 dl/g). Curves for these two polymers are shown in Figure 2. The slope of the curve for the endcapped polymer was about the same as the slope of the curve for the polymers prepared from oligocyclosilazanes, suggesting that inherently, the single cyclodisilazane ring is no less hydrolytically stable than the dimer or the tetramer.

One of the endcapped polymers was also examined for its thermogravimetric stability in dry air, both dynamically and isothermally. In the traces reproduced in Figures 3 and 4 some event, perhaps involving oxidation, occurred up to 350° as evidenced by a minor increase in weight. The knee indicating catastrophic thermal decomposition did not occur until above 500°. Time limitations precluded long period exposure under isothermal conditions at 260°, which would have provided the most direct information of the polymer's thermal stability. Therefore, 6-hr. isothermal thermograms were made at 40° increments between 260° and 460°.

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* All infrared spectra are reproduced in the Appendix, p. 63.

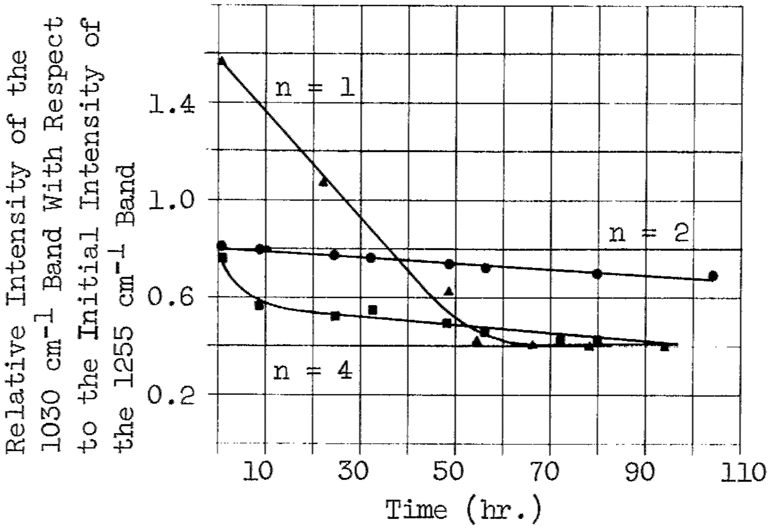


Figure 1 - Relative Hydrolytic Stabilities of Polymers Containing Cyclodisilazane Rings for Structures in Which n = 1, 2, and 4

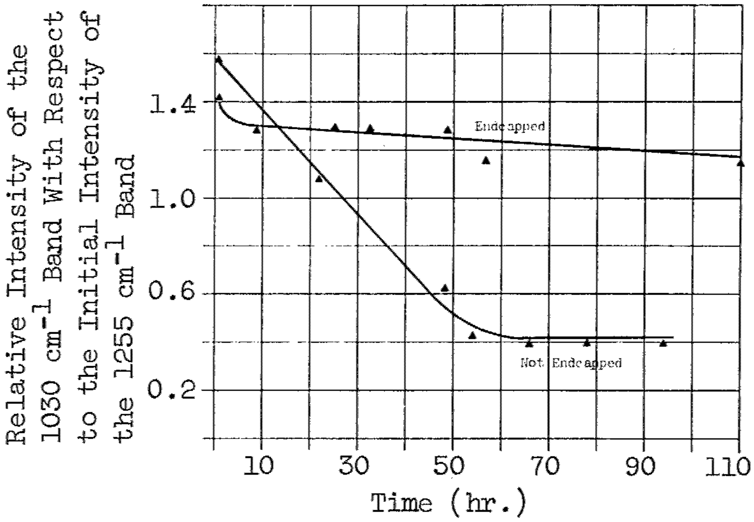
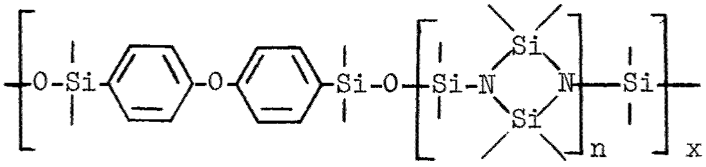


Figure 2 - Relative Hydrolytic Stabilities of Endcapped and Nonendcapped Polymers Containing Cyclodisilazane Rings (n = 1)



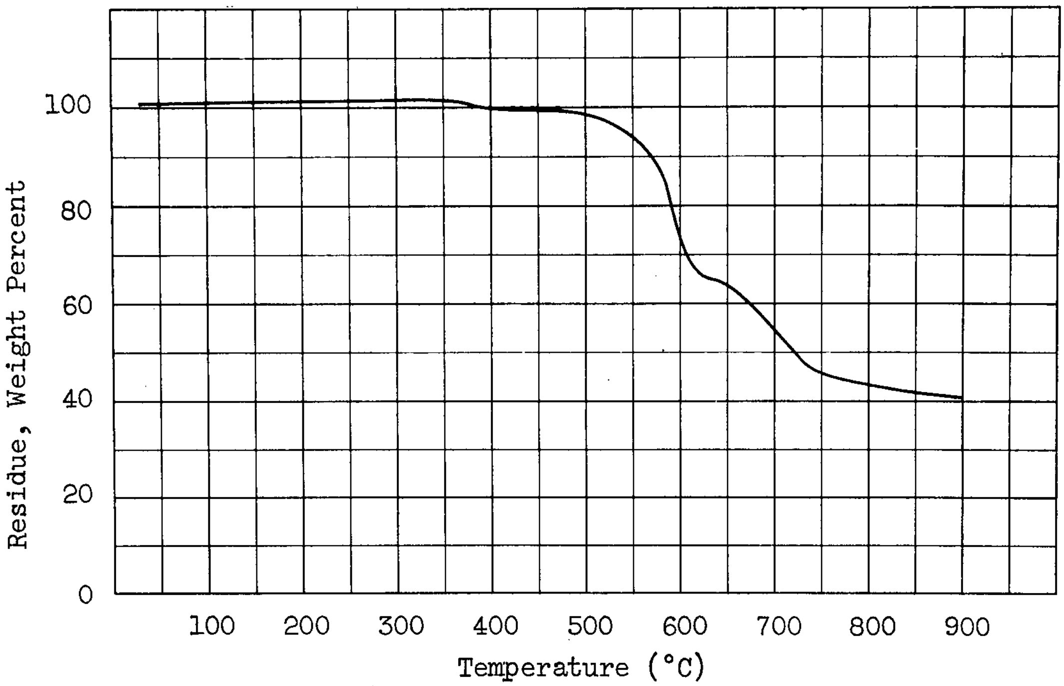


Figure 3 - Thermogravimetric Analysis of Polymer No. 4, Table VIII, p. 51 (Heating Rate, 3°C/min; Atmosphere, dry air)

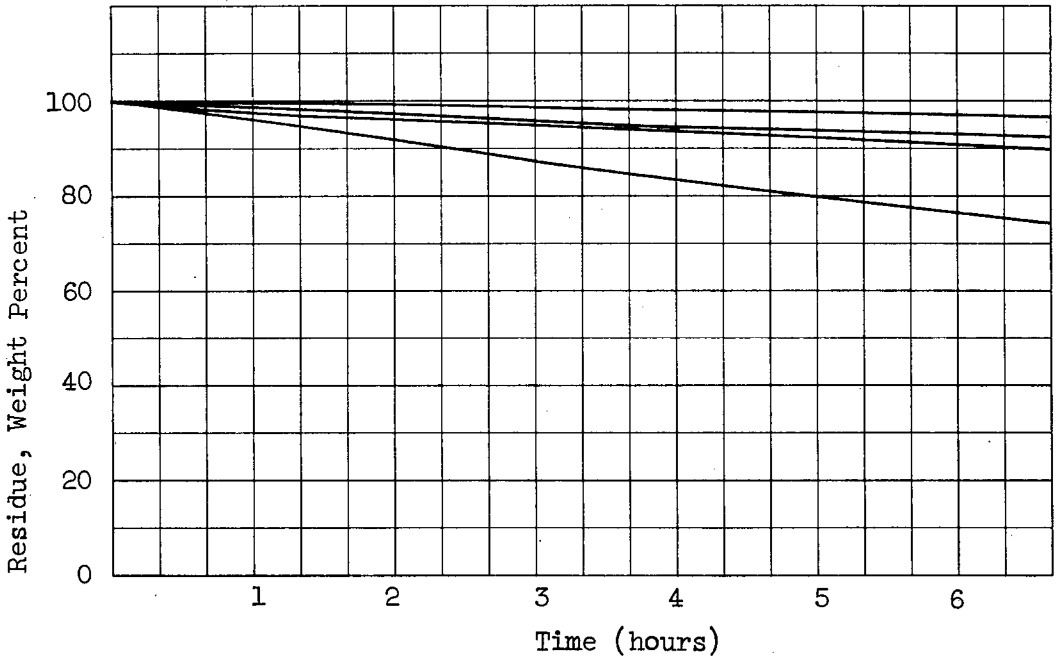


Figure 4 - Isothermal Thermogravimetric Analyses of Polymer No. 4, Table VIII, p. 51 (Atmosphere, dry air; from top to bottom, the traces were made at the following temperatures: 1, 260°; 2, 300°, 340°, and 380°; 3, 420°; and 4, 460°)

A low weight loss was observed at 260°. The traces at 300°, 340°, and 380° were superimposable, but represented a somewhat greater weight loss than at 260°. The rate of weight loss decreased somewhat after 4 hr. The rate of weight loss was just slightly greater at 420°, but became much more rapid at 460°. From these data it appears that the event that accounts for rapid thermal decomposition is initiated between 420° and 460°.

4. *Other condensation polymerizations*: Since higher molecular weight condensates with a lesser tendency to form crosslinked structures had been obtained with the substitution of diethylamine for the dimethylamine derivatives of the cyclodisilazane monomer, the possibility of further improving the polymeric compositions through the use of a leaving group with an even higher K_B was considered. N,N'-bis[dimethyl(piperidino)-silyl]tetramethylcyclodisilazane was therefore prepared and used in several of the polymerizations. The conditions used for the polymerizations were the same that had proved to be the optimum conditions for the diethylamine derivative and fairly low molecular weight condensates were obtained. In view of the fact that higher polymerization temperatures were required to obtain improved materials when the diethylamine derivative was substituted for the dimethylamine derivative in the condensates, yet higher temperatures may be required for the piperidine derivative condensates.

The incorporation of small percentages of *p*-phenylenebis(methylvinylsilanol) to provide crosslinking sites in compositions based on N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(*p*-hydroxydimethylsilylphenyl) ether resulted in a loss of solubility early in the polymerizations. This solubility loss can be attributed to the presence of the vinyl group because the usual polymer could be obtained when *p*-phenylenebis(dimethylsilanol) was used in place of *p*-phenylenebis-(methylvinylsilanol) in the compositions. The properties of the vinyl-containing monomer were further investigated by substituting an equivalent quantity of it in a condensation polymerization of *p*-phenylenebis(dimethylsilanol) and decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane. With these monomers, a polymer with an inherent viscosity of 0.72 dl/g was obtained, presumably incorporating the vinyl groups. Apparently, a possible interaction between the vinyl groups and the cyclodisilazane rings must be considered.

Because of its greater ease of preparation, some consideration was given to the use of *p*-phenylenebis(dimethylsilanol) in place of bis(*p*-hydroxydimethylsilylphenyl) ether in condensation reactions with N,N'-bis[(dialkylamino)dimethylsilyl]tetramethylcyclodisilazanes. However, this modifications seemed to uniformly give lower molecular weight polymers.

III.

FUTURE WORK

On the basis of the results in this report and earlier reports, it is recommended that future laboratory work include the following:

1. The development of methods to incorporate vinyl groups in the cyclodisilazane-arylene disilanol condensates in order to provide cross-linking sites.

2. The development of methods to incorporate 3,3,3-trifluoropropyl groups in the cyclodisilazane-arylene disilanol condensates in order to improve their fluid resistance.

3. The further investigation of the use of N,N'-bis[dimethyl(piperidino)dimethylsilyl]tetramethylcyclodisilazane as a monomer in the condensations with arylene disilanols in order to obtain higher molecular weight, soluble polymers.

4. Continue the investigation on the possible use of oligomeric cyclodisilazanes in polymeric compositions.

5. The investigation of the base-catalyzed linearization of 1,5-bis(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane to a polymer containing the trisilylamine structure.

6. The investigation of the use of metallated cyclosilazanes in the synthesis of new monomers.

IV.

EXPERIMENTAL

All chlorosilanes were redistilled before being used. Reactions were carried out in glass equipment that had been flame-dried and flushed with dry nitrogen before use. Reactants were protected from atmospheric moisture with Drierite-packed tubes or a positive pressure of dry nitrogen as needed. Elemental analyses were conducted by Spang Microanalytical Laboratory. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer and n.m.r. spectra were determined with a Varian Associates Model A60 spectrometer using cyclohexane as an internal standard.

A. Synthesis of Miscellaneous Organosilicon Monomers, Intermediates, and Samples

1. Chlorotriethylsilane: A solution of 146.0 g. (0.596 mole) of hexaethyldisilazane in 1 liter of ether was treated over a 3-hr. period with an excess of anhydrous hydrogen chloride. The mixture was cooled occasionally with an ice-water bath in order to maintain the temperature between 20° and 25°. After the mixture was refluxed for 1 hr. to expel excess hydrogen chloride, cooled, and filtered, 30.2 g. (94%) of ammonium chloride was filtered off. Distillation of the filtrate through a 30-cm. column gave 151.5 g. (85%) of chlorotriethylsilane boiling at 145-146° (reported, b.p. 143-145°) (Ref. 6).

2. Chlorotribenzylsilane: The procedure of Martin and Kipping was followed (Ref. 4). To 35.5 g. of a mixture of tribenzylsilanol and aminotribenzylsilane was added 333 g. (4.25 moles) of acetyl chloride and the mixture was refluxed for 3 hr. Excess acetyl chloride was evaporated and the residue was refluxed in 500 ml. of petroleum ether, b.p. 60-90°. Recrystallization of petroleum ether-insoluble portion from toluene afforded 28.1 g. (75%) chlorotribenzylsilane, m.p. 140-141° (reported 141°) (Ref. 7). The infrared spectrum is reported in Figure 5.

3. Triethylsilylamine: To a solution of 300 ml. of ammonia and 200 ml. of petroleum ether, b.p. 35-60°, cooled in a Dry Ice-isopropyl alcohol bath, was added 400 g. (2.66 moles) of chlorotriethylsilane dropwise in 2 hr. After adding another 200 ml. of petroleum ether, the mixture was stirred for 2 hr. at a temperature at which ammonia refluxed and then heated slowly to expel excess ammonia. A preliminary distillation after the ammonium chloride was filtered off and the solvent was distilled gave 344 g. of distillate boiling between 65° (atm. pressure) and 77° (1 mm.).

Redistillation on a 36-in. spinning band column gave the following fractions: 134 g. (39%) of triethylsilylamine, b.p. 137-138°, n_D^{20} 1.4270 (reported b.p. 134°, n_D^{20} 1.4267) (Ref. 6), and 133 g. (41%) of hexaethyldisilazane, b.p. 73-74° (1.0 mm.), n_D^{20} 1.4542 [reported b.p. 244-245° (atm.), n_D^{20} 1.4455] (Ref. 8), g.l.c. analysis (1-meter column packed with 5% SE-30 on 80/100 Chromport XXX, flow rate 50 ml. of N_2/min, 50° and 80°, respectively) indicated a major peak at 3.5 min. and a shoulder at 4.2 min. for the triethylsilylamine fraction, and 2 peaks, one at 8.0 min. (1.8%) and the other at 14.0 min. (98.2% for hexaethyldisilazane). The infrared spectrum of hexaethyldisilazane is reported in Figure 6.

Anal.(for aminotriethylsilane) Calcd. for $C_6H_{17}NSi$: C, 54.88; H, 13.05; N, 10.67; Si, 21.39. Found: C, 54.88; H, 13.02; N, 10.62; Si, 21.31.

Anal.(for hexaethyldisilazane) Calcd. for $C_{12}H_{31}NSi_2$: C, 58.71; H, 12.68; N, 5.71; Si, 22.88. Found: C, 58.61; H, 12.68; Si, 22.74.

In a second experiment which followed Bailey's procedure (Ref. 6), 210 ml. of ammonia was treated with 152 g. (1.01 moles) of chlorotriethylsilane in the same manner except that no solvent was used. After the ammonia was distilled, 200 ml. of dry ether was added and the ammonium chloride was filtered off. A preliminary distillation gave 111 g. of impure aminotriethylsilane, which was collected between 133 and 135° (atm.). Redistillation on a 36-in. spinning band column gave 99 g. (75%) of aminotriethylsilane, b.p. 137° (atm.), n_D^{20} 1.4265. G.l.c. analyses gave essentially the same results that had been obtained in the first experiment.

The two products were combined and fractionally redistilled on the spinning band column. Nine fractions, all boiling at 138° (atm.), weighed 216 g. G.l.c. analyses of all of the fractions showed the major peak at 3.5 min. with a shoulder at 4.2 min. The refractive index of the combined fractions was n_D^{20} 1.4268, and the infrared spectrum is reported in Figure 7.

4. Tribenzylsilylamine: To 123 ml. of ammonia, cooled in a Dry Ice-isopropyl alcohol bath, was added 41.4 g. (0.123 mole) of chlorotribenzylsilane as a slurry in 300 ml. of dry ethyl ether in 1 hr. The mixture was stirred at a temperature at which the ammonia refluxed for 2 hr. and then heated slowly to distill excess ammonia. After the ammonium chloride (6.0 g., 91%) was collected, evaporation of the solvent gave 39.3 g. of a solid residue. Two recrystallizations of this residue from petroleum ether, b.p. 60-90°, gave 30 g. of a mixture, m.p. 89-96°, of tribenzylsilylamine and tribenzylsilanol.

Anal. Calcd. for $C_{21}N_{23}NSi$: C, 79.44; H, 7.29; N, 4.41; Si, 8.85. Found: C, 80.00; H, 7.24; N, 3.30; Si, 8.94.

In a repetition of the experiment with 28.1 g. (0.086 mole) of freshly prepared chlorotribenzylsilane, m.p. 140-141°, the chlorosilane was added as a slurry in 400 ml. of dry ether to 95 ml. of condensed ammonia, which was cooled in an isopropyl alcohol-Dry Ice bath. After the mixture was stirred for 2 hr. at a temperature at which the ammonia refluxed, excess ammonia was distilled out. Filtration gave 4.2 g. (calcd., 4.4 g.) of ammonium chloride. Evaporation of the ether and recrystallization of the residue from petroleum ether, b.p. 60-90°, gave 23.5 g. of aminotribenzylsilane, m.p. 101-102° (d.t.a.).* A second 2.0 g.-fraction was recovered from the recrystallization solvent. The total conversion was 95%. The infrared spectrum is reported in Figure 8.

Anal. Calcd. for $C_{21}H_{23}NSi$: C, 79.44; H, 7.29; N, 4.41; Si, 8.85. Found: C, 79.12; H, 7.38; N, 4.29; Si, 8.47.

5. Aminotriphenylsilane: The procedure of Dannley and Jalics was followed (Ref. 9). After 58.9 g. (0.20 mole) of chlorotriphenylsilane in 200 ml. of dry ether was added over a 0.5-hr. period to 200 ml. of condensed ammonia, which was cooled in an isopropyl alcohol-Dry Ice bath, the mixture was stirred and the ammonia was allowed to reflux for 2.5 hr. Subsequently the ammonia was distilled and the ammonium chloride, 10.3 (calcd., 10.7 g.), was collected by filtration. Evaporation of the filtrate afforded 56.5 g. of unpurified aminotriphenylsilane.

Repetition of the experiment with 294.5 g. (1.00 mole) of chlorotriphenylsilane and 1,000 ml. of ammonia gave 295 g. of unpurified aminotriphenylsilane. After two recrystallizations of the combined products from petroleum ether, b.p. 60-90°, 251 g. (76%) of aminotriphenylsilane, m.p. 53-57° (reported 56-57°), (Ref. 9) was obtained.

Anal. Calcd. for $C_{18}H_{17}NSi$: C, 78.48; H, 6.22; N, 5.09; Si, 10.20. Found: C, 78.45; H, 6.23; N, 4.37; Si, 8.65.

When the 251 g. of the impure aminotriphenylsilane was heated in 3 liters of petroleum ether, b.p. 35-60°, and filtered, 36 g. of triphenylsilanol, which was identified by its infrared spectrum, was collected. After the filtrate was cooled, 117 g. of aminotriphenylsilane, m.p. 57-60°, crystallized.

Anal. Calcd. for $C_{18}H_{17}NSi$: C, 78.48; H, 6.22; N, 5.09; Si, 10.20. Found: C, 79.09; H, 6.16; N, 4.43; Si, 9.64.

After the liquid portion was concentrated to 1,350 ml. and cooled, 49 g. of aminotriphenylsilane, m.p. 58-62°, crystallized.

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* Throughout the report d.t.a. indicates differential thermal analysis.

Anal. Calcd. for $C_{18}H_{17}NSi$: C, 78.48; H, 6.22; N, 5.09; Si, 10.20. Found: C, 79.06; H, 6.18; N, 4.80; Si, 9.66.

When the volume of the remaining liquid was reduced to 600 ml. by evaporation and cooled, 20 g. of aminotriphenylsilane, m.p. 59-62°, was collected upon filtration.

Anal. Calcd. for $C_{18}H_{17}NSi$: C, 78.48; H, 6.22; N, 5.09; Si, 10.20. Found: C, 78.94; H, 6.17; N, 4.86; Si, 9.86.

A typical infrared spectrum, which is reported in Figure 9, indicates the absence of SiOH absorption that occurs at 3250 cm^{-1} in triphenylsilanol.

In a third experiment, freshly recrystallized chlorotriphenylsilane was used. The chlorotriphenylsilane showed a single peak on g.l.c. analysis (1-meter column packed with 5% SE-30 80/100 Chromport XXX, flow rate 50 ml. of N_2/min, 200°). To 500 ml. of condensed ammonia in an isopropyl alcohol-Dry Ice bath was added 132 g. (0.45 mole) of chlorotriphenylsilane in 500 ml. of dry ether over a 1-hr. period. The mixture was stirred and the ammonia was allowed to reflux for 2 hr. After the ammonia was distilled, ammonium chloride, 22.5 g. (calcd., 24 g.) was removed by filtration. Evaporation of solvent afforded 129 g. of crude aminotriphenylsilane. Recrystallization from petroleum ether, b.p. 35-60°, gave a total of 112 g. (91%) of aminotriphenylsilane in three fractions having the following melting point ranges: a, 54 g., m.p. 56-59°; b, 38 g., m.p. 56-59°; c, 20 g., m.p. 54-57° [reported, 56-57° (Ref. 9), 59-60° (Ref. 10)].

Anal. Calcd. for $C_{18}H_{17}NSi$: C, 78.48; H, 6.22; N, 5.09; Si, 10.20. Found for fraction a: C, 79.04; H, 6.13; N, 4.66; Si, 9.61. Found for fraction b: C, 78.94; H, 6.21; N, 4.78; Si, 9.64. Found for fraction c: C, 78.88; H, 6.19; N, 4.75; Si, 9.84.

In the melting of all six fractions, a small portion of each sample remained unfused and did not dissolve in the melt until about 90°.

6. Bis(p-ethoxydimethylsilylphenyl) ether: A solution of 700 g. (2.14 moles) of bis(p-bromophenyl) ether in 1.1 liters of dry tetrahydrofuran was added to 114.6 g. (4.72 g.-atoms) of previously activated magnesium covered with 200 ml. of dry tetrahydrofuran at a rate which maintained an exotheric reaction. After the addition was complete, the mixture was refluxed for 2 hr., treated with 634 g. (4.28 moles) of diethoxydimethylsilane over a period of 45 min., and then refluxed overnight. The mixture was filtered to remove the remaining magnesium, and the solvent was evaporated in a rotary evaporator. The residue was washed

exhaustively with petroleum ether, b.p. 60-90°, and the combined extracts were evaporated. A preliminary distillation of the residue gave 393.4 g. of a liquid, which was redistilled on a 36-in. spinning band column to obtain 301.7 g. (38%) of bis(p-ethoxydimethylsilylphenyl) ether, b.p. 137-138° (0.01 mm.), n_D^{20} 1.5210 [reported, b.p. 141-142° (0.1 mm.) n_D^{20} 1.5213] (Ref. 11).

7. Bis(p-hydroxydimethylsilylphenyl) ether: After 151 g. (0.40 mole) of bis(p-ethoxydimethylsilylphenyl) ether was added over a 20-min. period to a solution of 80.8 g. (2.02 moles) of sodium hydroxide in 383 ml. of methanol and 32 ml. of water, the solution was treated with 80.8 g. (2.02 moles) of sodium hydroxide in 315 ml. of water. After the solution was stirred for 3 hr., the resulting sodium salt was hydrolyzed by addition to 206.7 g. (1.52 moles) of potassium diacid phosphate in 1.5 liters of water and 1.5 kg. of ice over a 2-hr. period. The mixture was stirred for an additional hour, the precipitate was filtered off and mixed and subsequently filtered four times from 1-liter portions of distilled water. After the residue was dried under reduced pressure at 45° for 9 hr., 121.1 g. (95%) of bis(p-hydroxydimethylsilylphenyl) ether was obtained. The material was dissolved in a boiling solution of 330 ml. of petroleum ether, b.p. 60-90°, and 500 ml. of toluene, decanted from a small amount of insoluble material, and allowed to crystallize.

The first recrystallization gave 98.8 g. (78%) of bis-(p-hydroxydimethylsilylphenyl) ether, m.p. 94-104°. A second recrystallization from 440 ml. of toluene and 290 ml. of petroleum ether afforded 95.9 g. (75%) of bis(p-hydroxydimethylsilylphenyl) ether, m.p. 102-104° (d.t.a.).

In another experiment, 151 g. (0.40 mole) of bis(p-ethoxydimethylsilylphenyl) ether was treated similarly; however, the sodium salt was hydrolyzed with 274.7 g. (2.02 moles) of potassium diacid phosphate in 2 liters of water and 2 kg. of ice. The total weight of diol obtained was 123.2 g. (97%). Two recrystallizations gave 109.0 g. (85%) of bis(p-hydroxydimethylsilylphenyl) ether, m.p. 102-104° (d.t.a.).

A sample of bis(p-hydroxydimethylsilylphenyl) ether that had partially polymerized was purified in the following manner: The material, 19.8 g., was dissolved in a solution of 10.6 g. (0.26 mole) of sodium hydroxide and 200 ml. of 95% ethanol and the solution was heated on a steam bath for 1 hr. The cooled solution was added dropwise in 1 hr. to 38.0 g. (0.27 mole) of potassium diacid phosphate in 300 ml. of water and 300 g. of ice, which was rapidly stirred. The diol was filtered off, washed well with water, and air dried. Recrystallization from 100 ml. of petroleum ether, b.p. 60-90°, and 150 ml. of toluene gave 16.7 g. of bis(p-hydroxydimethylsilylphenyl) ether, m.p. 103-105° [dried at 70° (0.1 mm.) for 7 hr.], m.p. 102-103° (d.t.a).

8. Dimethylaminodimethylvinylsilane: A solution of 9.3 g. (0.20 mole) of freshly condensed dimethylamine in 200 ml. of petroleum ether, b.p. 35-60°, was cooled in a Dry Ice-isopropyl alcohol bath and treated with 12.5 g. (0.10 mole) of chlorodimethylvinylsilane in 50 ml. of petroleum ether. The mixture was stirred for 1 hr. at the Dry Ice-isopropyl alcohol bath temperature, slowly warmed to room temperature, and allowed to stand for 48 hr. After 8.5 g. (calcd. 8.4 g.) of dimethylamine hydrochloride was filtered off, fractional distillation gave 7.2 g. (53%) of dimethylaminodimethylvinylsilane, b.p. 109-110°, n_D^{20} 1.4189 (reported, b.p. 107°, n_D^{25} 1.4170) (Ref. 12).

B. Synthesis of Cyclodisilazane Monomers and Intermediates

1. N,N'Bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane: A solution of 80 ml. (excess) of dimethylamine in 250 ml. of petroleum ether, b.p. 35-60°, which was cooled in a Dry Ice-isopropyl alcohol bath, was treated with a solution of 98.8 g. (0.298 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 180 ml. of petroleum ether. After the addition was complete, the mixture was warmed to room temperature, the salts were filtered off, and the solvent was removed by distillation. The residue distilled on a 30-in. spinning band gave 67.2 g. (65%) of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane, b.p. 105° (2 mm.), n_D^{20} 1.4537-1.4538 [reported b.p., 122-123° (5 mm.), n_D^{20} 1.4530, AFML-TR-66-116, Part II , p. 35]. A g.l.c. analysis (1-meter column packed with 5% SF-96 on 100/120 mesh Gas Chrom Q, flow rate, 50 ml. of N_2/min, 150°) of a 21.3-g. fraction showed a single peak at 4.0 min. A 23.0-g. sample and a 22.9-g. fraction each showed about 99% purity.

When the 46 g. of impure N,N'-bis[(dimethylamino)dimethylsilyl]-tetramethylcyclodisilazane was redistilled through a 30-in. spinning band column, 33.9 g. of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane, b.p. 96-97° (2 mm.), that showed a single g.l.c. peak was obtained. A lower boiling fraction, 9.2 g., and 2.0 g. of a residue, was also obtained.

2. N,N'-Bis [(diethylamino)dimethylsilyl]tetramethylcyclodisilazane: To 31.9 g. (0.414 mole) of freshly distilled diethylamine in 150 ml. of petroleum ether, b.p. 60-90°, was added dropwise 259 ml. of 1.6 M n-butyllithium in hexane while the temperature was kept below 30°. The mixture was then treated with 68.5 g. (0.207 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 150 ml. of petroleum ether over a 1.5-hr. period, stirred for 0.5 hr. at room temperature, and heated at reflux for 2 hr. After the salts were filtered off and the solvent was evaporated, a preliminary distillation gave 56.8 g. of crude N,N'-bis-[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, b.p. 100-130°

(0.75 mm.). This crude product was combined with 5.5 g. of impure N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, b.p. 88-102° (0.47 mm.), from a previous synthesis and distilled on a spinning band column to obtain 38.2 g. of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, b.p. 107-109° (0.5 mm.), n_D^{20} 1.4590, g.l.c., a single peak at 2.1 min. (1-meter column packed with 5% SF-96 on 100/120 mesh Gas Chrom Q, 200°, N_2, 50 ml/min).[reported b.p. 164° (12 mm.), n_D^{20} 1.4584] (Ref. 13). The yield, correcting for the 5.5 g. of added N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, was 46%.

The g.l.c. data for this sample ultimately proved to be in error. After the monomer was used in a polymerization in which the polymer obtained had a solution viscosity no higher than 0.26 dl/g, the purity was redetermined and found to be 94.2% (1-meter column packed with 2% SF-96 on 100/200 mesh Gas Chrom Q, 165°, N_2, 50 ml/min). The 24.6 g. remaining was redistilled with the product of the following preparation.

In a repetition of the experiment with 55.7 g. (0.168 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, 68% of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, b.p. 100-101° (0.7 mm.), showing a single g.l.c. peak, was obtained. The total monomer obtained after two distillations of the combined products was 48.8 g.

Two additional replications of this experiment were carried out to obtain quantities of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane for use in polymerizations. One sample, b.p. 105-106° (0.6 mm.), was forwarded for elemental analyses.

Anal. Calcd. for $C_{16}H_{44}N_4Si_4$: C, 47.46; H, 10.95; N, 13.84; Si, 27.75. Found: C, 47.51; H, 10.80; N, 14.02; Si, 27.68.

3. N,N'-Bis[dimethyl(piperidino)silyl]tetramethylcyclodisilazane: To 10.2 g. (0.12 mole) of freshly distilled piperidine in 50 ml. of petroleum ether, b.p. 60-90°, was added dropwise 75.0 ml. (0.012 mole) of 1.6 M n-butyllithium in hexane while the temperature was kept below 30°. The mixture was then treated with 20.0 g. (0.061 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 50 ml. of petroleum ether over a 0.5-hr. period, stirred for 0.5 hr. at room temperature, and heated at reflux for 2 hr. After 6.9 g. (calcd. 5.1 g.) of lithium chloride was filtered off and the solvent evaporated, a vacuum distillation gave 17.8 g. (70%) of N,N'-bis[dimethyl(piperidino)silyl]tetramethylcyclodisilazane, b.p. 142-144° (0.10 mm.), m.p. 42-43° (sealed capillary tube), infrared spectrum, Figure 10, n.m.r. peaks ($CHCl_3$) at τ 10.02 [12H, singlet, pendant $Si(CH_3)_2$], τ 9.77 [12H, singlet, cyclodisilazane $Si(CH_3)_2$], τ 8.62 [12H, multiplet, piperidine $(CH_2)_3$], and τ 7.25 [8H, triplet, piperidine $(CH_2)_2N$].

Anal. Calcd. for $C_{18}H_{44}N_4Si_4$: C, 50.40; H, 10.34; N, 13.06; Si, 26.19. Found: C, 50.45; H, 10.20; N, 13.09; Si, 26.02.

After the material was redistilled through a spinning band column, g.l.c. analysis (2-meter column packed with 5% SF-96 on 100/120 Gas Chrom Q, flow rate 36 ml/min He, 225°) showed no impurities.

4. N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane: When the petroleum ether-soluble portion of the product of the equilibration of 129.0 g. (1.0 mole) of dichlorodimethylsilane and 146.0 g. (0.5 mole) of octamethylcyclotetrasilazane at 175°C for 72 hr. was distilled, the following fractions were obtained: a, b.p. 80-136° (45 mm.), 25.1 g.; b, 142-150° (45 mm.), 32.5 g.; c, 151-156° (45 mm.), 97.6 g.; d, 156-162° (45 mm.), 33.2 g.; and e, > 164° (45 mm.), 52.2 g. All except 5.6 g. of the higher boiling material distilled below 170° (0.05 mm.).

In another preparation with 159 g. (0.54 mole) of octamethylcyclotetrasilazane and 142 g. (1.10 mole) of dichlorodimethylsilane, 104 g. (38%) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, b.p. 150-153° (45 mm.) [reported 153-154° (46 mm.)] (Ref. 14), was collected.

A number of high- and low-boiling fractions from previous experiments as well as some recovered fractions were also combined and redistilled to obtain 71.6 g. of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, b.p. 148-160° (45 mm.). A number of higher boiling, but ill-defined, fractions were also separated in an attempt to obtain oligocyclodisilazanes, but each of these fractions proved to contain 4-9 g.l.c. peaks.

5. N,N'-Bis(anilinodimethylsilyl)tetramethylcyclodisilazane: To 4.2 g. (0.045 mole) of freshly distilled aniline in 50 ml. of anhydrous diethyl ether was added dropwise 28 ml. (0.045 mole) of 1.6 N n-butyllithium in hexane, while the temperature was kept below 30° with an ice bath, followed by 7.5 g. (0.022 mole) of N,N'-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane in 50 ml. of diethyl ether over a period of 0.5 hr. After the mixture was stirred another 0.5 hr. at room temperature, heated at reflux for 1.0 hr., cooled, and filtered through a Celite-packed filter funnel, 2.2 g. (calcd. 1.9 g.) of lithium chloride was obtained. Evaporation of the filtrate gave 10.4 g. of a residue, m.p. 85-100°, from which 6.5 g. (65%) of N,N'-bis(anilinodimethylsilyl)tetramethylcyclodisilazane, m.p. 104-106°, infrared spectrum, Figure 11 [reported m.p., 106-107°, AFML-TR-66-116 (III), p. 27], was obtained after it was recrystallized from petroleum ether, b.p. 60-90°.

6. N,N'-Bis(3-phenyltetramethyldisiloxanyl)tetramethylcyclodisilazane (attempted): A solution of 4.50 g. (0.0295 mole) of dimethylphenylsilanol and 3.89 g. (0.0148 mole) of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane in 5.0 ml. of xylene was added dropwise to a mixture of 0.100 g. (0.00416 mole) of sodium hydride in 10 ml. of xylene. Hydrogen evolution began immediately and continued until the solid sodium hydride had disappeared. After the mixture was refluxed until 650 ml. of hydrogen (calcd. 663 ml.) had been collected, cooled, and the xylene removed in a rotary evaporator, the 8.9 g. of yellow liquid residue was filtered to remove the 0.3 g. that separated after overnight storage. Vacuum distillation gave the following fractions: a, 3.0 g., b.p. 92-110° (0.12 mm.), n_D^{20} 1.4880; b, 1.1 g., b.p. 130-160° (0.09 mm.), n_D^{20} 1.4840; c, 0.4 g., b.p. 163° (0.09 mm.), n_D^{20} 1.4869; N,N'-bis(3-phenyltetramethyldisiloxanyl)-tetramethylcyclodisilazane has a b.p. of 178-180° (0.02 mm.) and n_D^{20} 1.4869 [AFML-TR-69-20 (I), p. 34].

C. Synthesis of Trisilylamines and Related Compounds

1. Bis(chlorodimethylsilyl)trimethylsilylamine: To a solution of 87.3 g. (0.30 mole) of hexamethyl-(*N*-trimethylsilyl)cyclotrisilazane in 300 ml. of ether was added 65.7 g. (1.80 moles) of hydrogen chloride in 400 ml. of ether over a 2-hr. period while the mixture was maintained at -60°. The mixture was warmed to room temperature, filtered, and the solvent was distilled. Fractional distillation afforded 40.0 g. (49%) of bis(chlorodimethylsilyl)trimethylsilylamine, b.p. 102-103° (12 mm.) [reported, 104-105° (12 mm.)] (Ref. 15).

2. Bis(diethylaminodimethylsilyl)trimethylsilylamine (attempted): While the temperature was kept below 30° with an ice bath, 84 ml. (0.134 mole) of 1.6 M *n*-butyllithium in hexane was added to 9.8 g. (0.134 mole) of diethylamine in 75 ml. of petroleum ether, b.p. 60-90°. After the addition was complete, 17.6 g. (0.064 mole) of bis(chlorodimethylsilyl)-trimethylsilylamine in 75 ml. of petroleum ether was added and the mixture was refluxed 2 hr. Filtration of the mixture through a Celite-packed funnel and distillation of the filtrate gave 13.8 g. of impure material boiling between 100-155° (7 mm.). Distillation of the 13.8 g. through a 30-in. spinning band column gave the following fractions: a, 2.8 g., b.p. 77-98° (6 mm.); b, 4.2 g., b.p. 98° (6 mm.); and c, 4.5 g., b.p. 98-109° (0.6 mm.).

The infrared spectrum (Figure 12) of fraction b showed CH_3CH_2 bands at 1040 and 920 cm^{-1} and a Si_2N band at 935 cm^{-1}. N.m.r. peaks (CCl_4) were observed at τ 10.00, τ 9.85, τ 9.76, τ 9.00 (triplet, J = 7 cps, CH_3), and τ 7.05 (quadruplet, CH_2). The observed proton ratio of CH_3CH_2

to $SiCH_3$ was 9:21, whereas the required ratio was 20:21 suggesting the fraction may have consisted chiefly of (chlorodimethylsilyl)(diethylaminodimethylsilyl)(trimethylsilyl)amine.

The experiment was repeated with essentially the same results. In an alternate procedure, diethylamine was used rather than the lithium salt.

A solution of 8.4 g. (0.030 mole) of bis(chlorodimethylsilyl)trimethylsilylamine in 30 ml. of pentane was added to 10.0 g. (0.137 mole) of diethylamine in 20 ml. of pentane in 0.3 hr., and the mixture was stirred at 27° for 2 hr. The mixture was freed from 0.5 g. of diethylamine hydrochloride salt by filtration. The filtrate developed an additional precipitate on standing and was again filtered to remove 1.0 g. of hydrochloride salt. After most of the solvent and excess diethylamine was distilled from the filtrate, 10 ml. of pentane was added, and the mixture was filtered again to remove 1.6 g. of salt (3.1 g. total, 47%). Short-path distillation gave 2.6 g. of a liquid, boiling range 58-71° (0.036 mm.) and additional precipitated salt. The material distilling initially solidified in the receiver. The residue, a mixture of hydrochloride salt and higher boiling liquid, weighed 1.4 g. The infrared spectrum of the distillate was similar to the spectrum of bis(chlorodimethylsilyl)trimethylsilylamine.

3. 1,3-Bis(diethylamino)tetramethyldisilazane: To a solution of 10.0 g. (0.050 mole) of 1,3-dichlorotetramethyldisilazane in 20 ml. of pentane was added dropwise 16.2 g. (0.22 mole) of diethylamine in 80 ml. of pentane while the reaction mixture was cooled by a Dry Ice-acetone bath. After the addition of the amine was complete, the mixture was allowed to warm to room temperature and then refluxed for 1 hr. After 9.7 g. (calcd., 10.9 g.) of diethylamine hydrochloride was filtered off and the filtrate was concentrated on a rotary evaporator at 25°, 11.0 g. of impure 1,3-bis-(diethylamino)tetramethyldisilazane was obtained. Distillation afforded 6.6 g. (48%) of the purified material, b.p. 104-108° (4.0 mm.), n_D^{20} 1.4448, infrared spectrum, Figure 13, n.m.r. peaks (CCl_4) at 9.95 (12H, singlet, $SiCH_3$), 9.06 (12H, triplet, CH_3), and 7.24 (8H, quadruplet, CH_2).

The compound, redistilled through a micro spinning band column, afforded 1.4 g. (44%) of 1,3-bis(diethylamino)tetramethyldisilazane, b.p. 103-104° (2.0 mm.), n_D^{20} 1.4442, which was submitted for elemental analysis.

Anal. Calcd. for $C_{12}H_{33}N_3Si_2$: C, 52.30; H, 12.07: N, 15.25; Si, 20.38. Found: C, 52.48; H, 11.62; N, 15.29; Si, 20.44.

4. 1-Trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane: While 8 ml. of ammonia was distilled into 15.5 g. (0.0566 mole) of bis(chlorodimethylsilyl)trimethylsilylamine in 150 ml. of pentane, the temperature of the mixture was maintained at 27° with a water bath. The mixture was filtered to remove 5.7 g. (calcd., 5.8 g.) of ammonium chloride, and the solvent was distilled from the filtrate under reduced pressure so as not to let the temperature of the product exceed 25°. The residue was then distilled similarly, and the distillate was collected in a Dry Ice trap. Fractional distillation of the material gave 9.4 g. (76%) of 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane, b.p. 60° (12 mm.) [reported, b.p. 55° (10 mm.)]; (Ref. 4) n.m.r. peaks (CCl_4) at τ 10.02 [9H, singlet, pendant $Si(CH_3)_3$] and τ 9.80 [12H, singlet, cyclodisilazane $Si(CH_3)_2$]. The infrared spectrum is reported in Figure 14.

5. 1,5-Bis(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane:

a. Attempted by the hydrolysis of 1-methyl-3-trimethylsilyl-2,2,4,4,-tetramethylcyclodisilazane: A mixture of 8.9 g. (0.0383 mole) of N-methyl-N'-trimethylsilyltetramethylcyclodisilazane, 0.40 g. (0.0223 mole) of water, and 75 ml. of pentane was stirred for three days. The water disappeared on the second day. The solution was decanted from a small amount of insoluble material, dried over anhydrous sodium sulfate, and the solvent was distilled off. Fractional distillation of the residue gave the following fractions: a, 3.2 g. (36%) of unchanged N-methyl-N'-trimethylsilyltetramethylcyclodisilazane, b.p. 60-61° (11 mm.); b, 0.3 g., boiling range 68-113° (5 mm.); c, 1.0 g., b.p. 136-141° (5 mm.); d, 0.8 g., b.p. 156-158° (0.27 mm.); and 2.4 g. of liquid residue.

b. By the hydrolysis of 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane: The procedure of Bush (Ref. 4) was followed in the hydrolysis of 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane. A mixture of 6.9 g. (0.032 mole) of 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane, 70 ml. of pentane, and 0.57 g. (0.0316 mole) of distilled water was stirred at intervals for three days. The water layer disappeared after 6 hr. After the solution was dried over sodium sulfate, the solvent was distilled. Fractional distillation of the residue gave 4.7 g. (68%) of 1,5-bis(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, of which 1.8 g. boiled at 145-147° (5 mm.), n_D^{20} 1.4562 and 2.9 g. boiling at 104° (0.05 mm.), n_D^{20} 1.4588. [Reported b.p. 126° (5 mm.), n_D^{22} 1.4571] (Ref. 4); infrared spectrum, Figure 15, n.m.r. peaks (CCl_4) at τ 9.82 [24H singlet, $Si(CH_3)_2$] and τ 9.86 [18H, singlet, $Si(CH_3)_3$].)

Anal. Calcd. for $C_{14}H_{42}N_2O_2Si_6$: C, 38.30; H, 9.64; N, 6.38; Si, 38.39. Found: C, 38.94; H. 9.50; N, 6.59; Si, 38.90.

6. Polymerization of 1,5-bis(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane: A mixture of 0.5 g. (0.00114 mole) of 1,5-bis(trimethylsilyl)-2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane and 0.0050 g. (1%) of tetramethylammonium hydroxide (dried at room temperature at 0.1 mm. for 1 hr.) was stirred at room temperature with a magnetic stirrer. The mixture solidified within 7 min. After it was stored for 16 hr., the inherent viscosity was 0.004 dl/g. The infrared spectrum did not differ greatly from the spectrum of the monomer.

D. Syntheses of 3,3,3-Trifluoropropyl- and Vinyl-Substituted Organosilicon Monomers and Intermediates

1. Diethoxymethylvinylsilane: A solution of 69 g. (1.50 moles) of ethanol and 119 g. (1.42 moles) of pyridine was added dropwise to a stirred solution of 100 g. (0.71 mole) of dichloromethylvinylsilane in 500 ml. of petroleum ether, b.p. 35-60°. During the addition, which required 1.5 hr., the temperature of the mixture was maintained between 15-20° with an ice bath. After the mixture was stored overnight at room temperature, the pyridine hydrochloride salt, 168.9 g. (calcd., 165.0), was filtered off and the filtrate was concentrated on a rotary evaporator at 30°. Vacuum distillation afforded 76.1 g. (67%) of diethoxymethylvinylsilane, b.p. 132°, n_D^{20} 1.4006; infrared spectrum, Figure 16 (reported, b.p. 133-134°, n_D^{20} 1.4000) (Ref. 15). In a repetition of the experiment, the yield was 77%.

2. p-Phenylenebis(ethoxymethylvinylsilane): A solution of 50 g. (0.21 mole) of p-dibromobenzene in 110 ml. of dry tetrahydrofuran was added in rapid drops to 10.5 g. (0.24 g.-atom) of previously activated magnesium covered with 20 ml. of tetrahydrofuran. The reaction proceeded exothermally until the addition of the p-dibromobenzene solution was complete. The mixture was then refluxed for 2 hr., treated with 69 g. (0.43 mole) of diethoxymethylvinylsilane, and again refluxed for 2 hr. After the mixture was cooled to room temperature, filtered, and the solvent distilled on a rotary evaporator, the semi-solid residue was exhaustively extracted with petroleum ether, b.p. 60-90°. The combined extracts, concentrated on a rotary evaporator, were vacuum distilled and 31.1 g. (48%) of p-phenylenebis(ethoxymethylvinylsilane) was obtained, b.p. 140° (2.0 mm.), n_D^{20} 1.4962, infrared spectrum, Figure 17.

Anal. Calcd. for $C_{16}H_{26}O_2Si_2$: C, 62.68; H, 8.55; Si, 18.33. Found: C, 62.85; H, 8.09; Si, 18.36.

3. p-Phenylenebis(hydroxymethylvinylsilane): A solution of 6.1 g. (0.002 mole) of p-phenylenebis(ethoxymethylvinylsilane) in 6.0 ml. of

95% ethanol was added to a stirred solution of 4.0 g. (0.10 mole) of sodium hydroxide in 14.0 ml. of methanol and 1.3 ml. of water. To this mixture was added a solution of 4.0 g. (0.10 mole) of sodium hydroxide in 15.3 ml. of water. After 1 hr., the solution was added dropwise to a vigorously stirred mixture of 80 g. of ice, 80 ml. of water, and 20.7 g. (0.15 mole) of monobasic potassium phosphate. After the mixture was slowly warmed to room temperature, the precipitated solids were filtered off, washed with water, air dried for two days, and vacuum dried for 2 hr. at 48°. The 4.9 g. (98%) of impure p-phenylenebis(hydroxymethylvinylsilane), m.p. 95-96°, had an infrared spectrum consistent with the structure.

A solution of 23.5 g. (0.077 mole) of p-phenylenebis(ethoxymethylvinylsilane) in 23 ml. of 95% ethanol was treated sequentially with 15.5 g. (0.39 mole) of sodium hydroxide in 54.0 ml. of methanol and 5.0 ml. of water and a solution of 15.5 g. (0.39 mole) of sodium hydroxide in 59.0 ml. of water. After 1 hr., the solution was added dropwise to a vigorously stirred mixture of 308 g. of ice, 308 ml. of water, and 80.0 g. (0.59 mole) of monobasic potassium phosphate. After the mixture was slowly warmed to room temperature, the precipitated solids were filtered off, washed with water, air dried for one day, and vacuum dried for 2 hr. at 48°. Recrystallization of this material from 120 ml. of toluene gave 15.4 g. (80%) of p-phenylenebis(hydroxymethylvinylsilane), m.p. 91-93° (d.t.a.), 96-97° (capillary); infrared spectrum, Figure 18; n.m.r. peaks (DMSO) at τ 9.57 (6H, singlet $SiCH_3$), τ 3.87 (6H, multiplet, $SiCH=CH_2$), τ 3.56 (singlet, SiOH), and τ 2.39 (4H, singlet, SiC_6H_5).

Anal. Calcd. for $C_{12}H_{18}O_2Si_2$: C, 57.55; H, 7.24; Si, 22.43. Found: C, 57.50; H, 7.26; Si, 22.31.

4. Bis(p-ethoxymethylvinylsilylphenyl) ether: A solution of 69.0 g. (0.21 mole) of bis(p-bromophenyl) ether in 110 ml. of dry tetrahydrofuran was added in rapid drops to 10.5 g. (0.24 g.-atom of previously activated magnesium covered with 20 ml. of tetrahydrofuran. The reaction proceeded exothermally until the addition of the bis(p-bromophenyl) ether solution was complete. The mixture was refluxed for 2 hr., treated with 69.0 g. (0.43 mole) of diethoxymethylvinylsilane, and again refluxed for 2 hr. After the mixture was cooled to room temperature, filtered, and the solvent distilled on a rotary evaporator, the semi-solid residue was exhaustively extracted with petroleum ether, b.p. 60-90°. The combined extracts, concentrated on a rotary evaporator, were vacuum distilled to give 29.3 g. (35%) of bis(p-ethoxymethylvinylsilylphenyl) ether, b.p. 192-194° (0.05 mm.); n_D^{20} 1.5320; infrared spectrum, Figure 19.

Anal. Calcd. for $C_{22}H_{30}O_3Si_2$: C, 66.28; H, 7.59; Si, 14.09. Found: C, 65.78; H, 7.29; Si, 14.59.

5. Bis(p-hydroxymethylvinylsilylphenyl) ether: A solution of 29.3 g. (0.0740 mole) of bis(p-ethoxymethylvinylsilylphenyl) ether in 25.0 ml. of 95% ethanol was added to a stirred solution of 15.4 g. (0.385 mole) of sodium hydroxide in 54.0 ml. of methanol and 5.0 ml. of water. To this mixture was added a solution of 15.4 g. (0.383 mole) of sodium hydroxide in 59.0 ml. of water. After 1 hr., the solution was added dropwise to a vigorously stirred mixture of 300 g. of ice, 300 ml. of water, and 80.0 g. (0.590 mole) of monobasic potassium phosphate. The mixture was slowly warmed to room temperature, the oily product separated by decantation, and dissolved in 55 ml. of petroleum ether, b.p. 60-90°, and 83 ml. of toluene. After storage at 0-4° for several days the solvent was removed on a rotary evaporator to give 26.3 g. of a viscous oil. All attempts to crystallize the product have failed. After the material was stored, first over pentane then over petroleum ether, b.p. 60-90°, the infrared spectrum (Figure 20) and the n.m.r. spectrum [peaks (DMSO) at τ 9.52 (6H, singlet, $SiCH_3$), τ 3.82 (6H, multiplet, $SiCH{=}CH_2$), τ 3.52 (singlet, SiOH), τ 2.90 (4H, doublet, C_6H_5), and τ 2.33 (4H, doublet, SiC_6H_5)] were consistent with the structure.

6. 2,4,6-Trimethyl-2,4,6-trivinylcyclotrisilazane: A solution of 81.0 g. (4.8 moles) of condensed ammonia in 800 ml. of petroleum ether, b.p. 60-90°, was cooled in a Dry Ice-isopropyl alcohol bath and treated with 141.0 g. (1.0 mole) of dichloromethylvinylsilane (b.p. 93°) dissolved in 400 ml. of petroleum ether. The addition required 1.0 hr. The mixture was then slowly warmed to room temperature and stored for two days. Ammonium chloride, 116.6 g. (2.1 moles), was filtered off and the solvent was distilled at 40° on a rotary evaporator. Vacuum distillation of the residue gave 67.4 g. (80%) of 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane, b.p. 100-102° (6.0 mm.), n_D^{20} 1.4840; infrared spectrum, Figure 21 [reported, b.p. 63-65° (1 mm.), n_D^{20} 1.482] (Ref. 17).

7. 2,4,6-Trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane: A solution of 21.1 g. (0.10 mole) of dichloromethyl(3,3,3-trifluoropropyl)silane (redistilled, b.p. 122-124°) in 60 ml. of petroleum ether, b.p. 35-60°, was added dropwise, over a period of 1 hr., to 15.4 g. (0.91 mole) of condensed ammonia dissolved in 160 ml. of petroleum ether and cooled by a Dry Ice-isopropyl alcohol bath. After the addition of dichloromethyl(3,3,3-trifluoropropyl)silane was completed, the mixture was slowly warmed to room temperature and 9.1 g. (calcd., 10.7 g.) of ammonium chloride was filtered off. The solvent was evaporated and the residue vacuum distilled to obtain the following fractions: a, 5.2 g., b.p. 130-144° (1.5 mm.), n_D^{20} 1.4060; b, 1.2 g., b.p. 141° (0.14 mm.), n_D^{20} 1.4052; and c, 2.9 g., b.p. 175-209° (0.02 mm.), n_D^{20} 1.4080. During

the distillation, some decomposition may possibly have occurred; therefore, in the following experiment the product was recrystallized.

In a second experiment with the same molar quantities, the residue that was obtained after the solvent was distilled off was refrigerated overnight and then allowed to stand at room temperature for three days. The liquid portion, 5.2 g., was decanted off to afford 11.3 g. of crude 2,4,6-2,4,6-trimethyltris(3,3,3-trifluoropropyl)cyclotrisilazane. This material was twice recrystallized from 5 ml. of pentane to obtain 6.6 g. (43%) of 2,4,6-trimethyltris(3,3,3-trifluoropropyl)cyclotrisilazane, m.p. 41-45° (reported, m.p. 74-82°) (Ref. 5). On differential thermal analysis, the recrystallized material showed a normal boiling point of 290-294° and no decomposition below this temperature.

Redistillation of various fractions of 2,4,6-trimethyl-2,4,6-tris-(trifluoropropyl)cyclotrisilazane gave 14.0 g., b.p. 134-136° (1.0 mm.), m.p. 41-45°, n_D^{20} 1.4073 (supercooled liquid); infrared spectrum, Figure 22; n.m.r. peaks (CCl_4) at τ 9.98 (9H, singlet, $SiCH_3$), τ 9.27 (6H, multiplet, $SiCH_2$), and τ 8.02 (6H, multiplet, CF_3CH_2).

Anal. Calcd. for $C_{12}H_{24}F_9N_3Si_3$: C, 30.95; H, 5.20; F, 36.73; N, 9.02; Si, 18.10. Found: C, 31.10; H, 5.18; F, 36.69; N, 8.89; Si, 18.04.

Another preparation with 42.2 g. (0.200 mole) of dichloromethyl-(3,3,3-trifluoropropyl)silane gave 18.1 g. (59%) of 2,4,6-tris(3,3,3-trifluoropropyl)-2,4,6-trimethylcyclotrisilazane, b.p. 115-116° (0.06 mm.), m.p. 38-44°, n_D^{20} 1.4044.

E. Synthesis of Phenyl-Substituted Organosilicon Monomers and Intermediates

1. 2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilazane: A solution of 100 ml. of condensed ammonia in 800 ml. of petroleum ether, b.p. 60-90°, cooled in a Dry Ice-isopropyl alcohol bath, was treated with 191 g. (1.0 mole) of dichloromethylphenylsilane dissolved in 400 ml. of petroleum ether in 0.75 hr. The mixture was allowed to warm to room temperature. After the salts were filtered off and the solvent was evaporated, distillation of the residue gave 121.4 g. (91%) of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane, b.p. 195-197° (0.05 mm.), [reported b.p. 193-195° (0.5 mm.), AFML-TR-66-116, Part II, p. 28]. The material partially crystallized on standing. The infrared spectrum is reported in Figure 23.

2. 1,3-Dichloro-1,3-diphenyl-1,3-dimethyldisilazane:

a. By the equilibration of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane and dichloromethylphenylsilane (1:3 mole ratio): A liquid sample of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane from which some of the solid isomer has been removed was used in this experiment. The cyclotrisilazane had been obtained in the boiling range of 193-195° (0.5 mm.) and showed two peaks on g.l.c. with an area ratio of 87:13 (1-meter column packed with 5% SE-30 on 80/100 mesh Chromport XXX, with nitrogen carrier, flow rate 50 ml. of N_2/min, 200°). After 20.3 g. (0.050 mole) of the cyclotrisilazane and 28.7 g. (0.150 mole) of dichloromethylphenylsilane were heated at 175° for 7 hr. and distilled, fractions were obtained in the following boiling ranges: a, 82-110° (13 mm.), 13.6 g.; b, 130-164° (0.3 mm.), 13.7 g.; and c, 196-230° (0.2 mm.), 10.6 g. Redistillation of fraction b, gave distillate in the following boiling ranges: a', below 48° (0.2 mm.), 3.1 g.; b', 115-125° (0.2 mm.), 6.0 g.; c', 134-136° (0.2 mm.), and d', 146-192° (0.2 mm.), 1.8 g. Fraction a was identified by g.l.c. as being chiefly recovered dichloromethylphenylsilane (47% recovery). The n.m.r. spectrum (carbon tetrachloride of fraction c') contained peaks consistent with the structure of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane: τ 9.45 and τ 9.33 (6H total, two singlets, $SiCH_3$), and τ 2.22-2.77 (10H, multiplet, SiC_6H_5).

b. By the cleavage of 2,4,6-trimethyl-2,4,6 triphenylcyclotrisilazane with hydrogen chloride: To a solution of 21.9 g. (0.0542 mole) of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane in 150 ml. of dry ether in an isopropyl alcohol-Dry Ice bath was added 11.8 g. (0.33 mole) of hydrogen chloride in 150 ml. of ether dropwise in 1.4 hr. After the mixture was stirred for 1 hr., it was allowed to warm up to room temperature. Ammonium chloride, 7.3 g. (calcd., 5.7 g.), was collected by filtration, and the filtrate was concentrated. Distillation of the residue through a 15-cm. unpacked column gave four fractions with the following boiling point ranges: a, 7.1 g., b.p. 86-87° (14 mm.); b, 7.3 g., b.p. 133-158° (0.2 mm.); c, 1.2 g., b.p. 185-200° (0.1 mm.); and d, 1.0 g., b.p. 200-214° (0.1 mm.).

c. By the condensation of dichloromethylphenylsilane with ammonia: To a solution of 38.2 g. (0.20 mole) of dichloromethylphenylsilane in 400 ml. of petroleum ether, b.p. 35-60°, in an isopropyl alcohol-Dry Ice bath was added 5.1 g. (0.30 mole) of ammonia. The mixture was stirred while it was allowed to warm up to room temperature. Ammonium chloride, 11.4 g. (calcd., 10.7 g.) was collected by filtration and the filtrate, after the solvent was evaporated was fractionally distilled under reduced pressure to obtain four fractions with the following boiling ranges: a, 10.0 g., b.p. 84-92° (13 mm.); b, 6.5 g., b.p. 140-150° (0.3 mm.); c, 1.3 g., b.p. 168-182° (0.2 mm.); d, 2.5 g., b.p. 194-224° (0.2 mm.); and 2.0 g. of residue.

d. Redistillation of combined products: When the products from the previous experiments that boiled in the range of 131-184° (0.2 mm.) were combined and redistilled, the following fractions were obtained: a, 1.5 g., b.p. 48-50° (0.5 mm.); b, 4.3 g., b.p. 130-132° (0.2 mm.); c, 2.6 g., b.p. 134-137° (0.2 mm.); d, 2.9 g., b.p. 137-140° (0.2 mm.); e, 0.5 g., b.p. 141-144° (0.2 mm.); f, 1.7 g., b.p. 154-170° (0.08 mm.); and 2.1 g. of residue. The infrared spectrum of fraction c was consistent with the structure of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane.

e. By the equilibration of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane and dichloromethylphenylsilane (1:4 mole ratio): The cyclotrisilazane reported in paragraph IV.E.1. was used in this experiment. A mixture of 20.3 g. (0.05 mole) of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane and 38.2 g. (0.20 mole) of dichloromethylphenylsilane was maintained at a temperature of 180° for 16 hr. Vacuum distillation of this mixture afforded 15.9 g. (33%) of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane, b.p. 158-160° (0.19 mm.); infrared spectrum, Figure 24; n.m.r. peaks (CCl_4) at τ 9.44 and 9.33 (6H, singlets, $SiCH_3$), τ 9.01 (1H, singlet, SiNH), and τ 2.26-2.74 (10H, multiplet, SiC_6H_5).

Anal. Calcd. for $C_{14}H_{17}Cl_2NSi_2$: C, 51.52; H, 5.25; N, 4.29; Si, 17.21. Found: C, 51.35; H, 5.32; N, 4.26; Si, 16.92.

3. N,N'-Bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (attempted): A solution of 15.0 g. (0.050 mole) of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane in 70 ml. of diethyl ether was added dropwise to a stirred solution of 8.5 g. (0.050 mole) of sodium bis(trimethylsilyl)amide in 125 ml. of diethyl ether. After the mixture was stirred for 2 hr. at room temperature and then filtered under a nitrogen atmosphere, 3.5 g. (calcd., 2.8 g.) of sodium chloride was obtained. The solvent was removed from the filtrate in a rotary evaporator and the residue was vacuum distilled to obtain the following fractions: a, 3.7 g., b.p. 150-165° (0.05 mm.); b, 7.5 g., b.p. 192-198° (0.04 mm.); infrared spectrum, Figure 25; n.m.r. peaks (CCl_4) at τ 9.81 (18H, singlet, $SiCH_3$), τ 9.53 (3H, singlet, $SiCH_3$), and τ 2.30-2.84 (10H, multiplet, SiPh); and c, 1.8 g., b.p. 204-217° (0.04 mm.).

In order to characterize the product, an attempt was made to convert it to the dimethylamine derivative. A solution of 9.3 g. (0.02 mole) of the compound tentatively identified as N,N'-bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (fractions b and c above) in 30 ml. of petroleum ether, b.p. 60-90°, was added dropwise to a solution of 3.5 g. (0.080 mole) of condensed dimethylamine in 40 ml. of petroleum ether which was cooled with a Dry Ice-isopropyl alcohol bath. After the addition of the solution was complete, the mixture was slowly warmed to room temperature and filtered to remove 0.7 g. (calcd., 2.8 g.) of dimethylamine hydrochloride. After the filtrate was concentrated on a rotary evaporator, the residue was fractionally distilled to obtain the following fractions: a, 1.4 g., b.p. 178-190° (0.27 mm.); b, 4.2 g., b.p. 191-192° (0.25 mm.), n_D^{20} 1.5370; infrared spectrum, Figure 26, n.m.r. peaks (CCl_4) at τ 9.84 (36H, singlet, $SiCH_3$), τ 9.54 (6H, singlet, $SiCH_3$), and τ 2.09-2.76 (10H, multiplet, SiC_6H_5); and c, 0.9 g., b.p. 194-198° (0.24 mm.), n_D^{20} 1.5382. The n.m.r. spectrum of fraction b did not show any $N(CH_3)_2$ resonance. Fraction b gave a satisfactory elemental analysis for 1,3-bis-[bis(trimethylsilyl)amino]1,3-dimethyl-1,3-diphenyldisilazane.

Anal. Calcd. for $C_{26}H_{52}N_3Si_6$: C, 54.29; H, 9.11; N, 7.30; Si, 29.30. Found: C, 55.06; H, 9.29; N, 7.16; Si, 28.56.

4. Equilibration of dichloromethylphenylsilane and N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane: Dichloromethylphenylsilane, 17.2 g. (0.090 mole), and 7.7 g. (0.023 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane were placed in a thermowell flask equipped with a microcolumn and distillation head. After the solution was heated under nitrogen to 204° in a Wood's metal bath, 1.2 g. of dichlorodimethylsilane, b.p. 72-75°, distilled over a 2-hr. period as the reflux temperature increased from 204 to 209°. No more dichlorodimethylsilane was collected during a 48-hr. heating period while the reflux temperature varied between 209 to 211°.

The residue was dissolved in 25 ml. of petroleum ether, b.p. 35-60°, and added to 25 ml. (excess) dimethylamine in 50 ml. of petroleum ether over a 0.5-hr. period while the mixture was maintained at -60°. The mixture was warmed to room temperature, filtered, and the solvent was distilled. Fractional distillation gave: a, 11.8 g. (63%) of bis(dimethylamino)methylphenylsilane, b.p. 107-110° (11 mm.), n.m.r. peaks (CCl_4) at τ 9.76 (3H, singlet, $SiCH_3$), τ 7.49 [12 H, singlet, $N(CH_3)_2$], and τ 2.41-2.81 (5H, multiplet, C_6H_5); b, 2.0 g., boiling range 115-128° (11 mm.); c, 1.1 g. of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane with some bis(dimethylamino)methylphenylsilane, b.p. 120-123° (5 mm.); and d, 2.3 g., b.p. 120-124° (0.1 mm.). There was 3.5 g. of liquid residue. The infrared and n.m.r. spectra of fraction c showed peaks present for both bis(dimethylamino)methylphenylsilane and N,N'-bis[(dimethylamino)dimethylsilyl] tetramethylcyclodisilazane. The infrared spectrum of fraction b was consistent with the assigned structure.

The infrared spectra of fraction d (Figure 27) and the residue showed bands at 1110 cm^{-1} (SiC_6H_5), 1030 cm^{-1} and 875 cm^{-1} (cyclodisilazane) and 980 cm^{-1} [$N(CH_3)_2$]. The n.m.r. spectra show a complex series of peaks in the $SiCH_3$ region (τ 9.41 to τ 10.18) with strong peaks at τ 10.02 [pendant $Si(CH_3)_2$] and τ 9.78 [cyclodisilazane ring $Si(CH_3)_2$], three peaks for $N(CH_3)_2$ at τ 7.71, τ 7.57, and τ 7.46, and peaks at τ 2.32-2.73 (SiC_6H_5). The proton ratios of C_6H_5:$SiCH_3$:NCH_3 were 14:68:39, indicating about one phenyl per molecule.

F. Equilibration Reactions

1. Thermal disproportionation of N,N'-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane (attempted): N,N'-Bis(chlorodimethylsilyl)-tetramethylcyclodisilazane, 6.8 g. (0.021 mole), b.p. 154° (45 mm.), was placed in a thermowell flask equipped with a microcolumn and microhead and heated under nitrogen at 245° for 240 hr.; no dimethyldichlorosilane distilled.

2. Aluminum chloride-catalyzed disproportionation of N,N'-bis-(chlorodimethylsilyl)tetramethylcyclodisilazane: After a mixture of 6.0 g. (0.018 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (99% g.l.c. pure) and 0.06 g. (1 wt %) of aluminum chloride was heated at 240° for 21 hr., 1.8 g. (calcd., 2.3 g.) of dichlorodimethylsilane and 3.9 g. of a brownish solid residue were obtained. The residue was readily soluble in toluene. Half of the residue in 12 ml. of toluene was treated with 0.5 g. of solid sodium chloride, filtered, and the toluene was evaporated. The infrared spectrum had not changed. The other half of the residue in 12 ml. of toluene was treated with 10 ml. of 1% sodium hydroxide solution, but an emulsion formed that could not be separated.

In a second experiment, when a mixture of 9.0 g. (0.027 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (97% pure by g.l.c.) and 0.09 g. (1 wt %) of aluminum chloride was heated to 235° in 4 hr., 2.6 g. (calcd., 3.5 g.) of dichlorodimethylsilane distilled. The residue in 25 ml. of toluene was treated with 0.5 g. of solid sodium chloride, filtered, and the toluene was evaporated. When the residue was heated to 260° (0.1 mm.), no distillate was collected. The infrared spectrum of the residue (4.2 g.) is reported in Figure 28.

A repetition of the experiment with 9.1 g. (0.027 mole) of N,N'-bis-(chlorodimethylsilyl)tetramethylcyclodisilazane and 0.0182 g. (0.2 wt %) of aluminum chloride gave 1.3 g. (calcd., 3.6 g.) of dichlorodimethylsilane after the mixture was heated at 140° for 6 hr. The residue was similarly treated with sodium chloride. When the residue was heated, 4.2 g. of distillate was collected between 80° (0.2 mm.) and 175° (0.1 mm.), which was a mixture of a solid and a liquid. The infrared spectrum of the solid is reported in Figure 29 and the liquid in Figure 30.

When a mixture of 8.7 g. (0.026 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (97% pure by g.l.c.) and 0.087 g. (1 wt %)

of aluminum chloride was heated at 240° for 8 hr., 2.6 g. of a liquid distilled, which according to g.l.c. analysis was predominantly dichlorodimethylsilane, but contained some chlorotrimethylsilane and some trichloromethylsilane (1-meter column, 5% SF-96 on Gas Chrom Q, 30°, 50 ml/min N_2 carrier gas). The portion of the 6.0 g. of brittle residue that was soluble in petroleum ether, b.p. 60-90°, was added to excess dimethylamine in 20 ml. of petroleum ether, which was cooled in an isopropyl alcohol-Dry Ice bath. After the salts were filtered off and the filtrate was concentrated, distillation in a short-path apparatus gave 0.2 g. of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane, which was identified by its infrared spectrum, when the residue was heated to 105° (0.5 mm.). The 4.5 g. of brittle solid residue was not completely soluble in toluene. It was soluble to the extent of 73% in petroleum ether, and the soluble portion had an inherent viscosity of 0.02 dl/g (0.5% in toluene, 30°) and ill-defined n.m.r. peaks (CCl_4) at τ 10.00, 9.78, 9.70, and 7.58.

3. <u>Equilibration of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane and hexamethylcyclotrisilazane (3:1 and 2:1 mole ratio)</u>: In one experiment, a mixture of 9.1 g. (0.0275 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (96% pure by g.l.c.) and 2.0 g. (0.0091 mole) of hexamethylcyclotrisilazane was heated at 175° for 48 hr. After the heating period, the residue was distilled in a short-path apparatus and a distillate (8.3 g., 75%) was collected between 125° (14 mm.) and 148° (3 mm.). The residue weighed 1.5 g. The composition of the distillate determined by g.l.c. is reported as experiment No. 1 in Table I.

In a second experiment, 8.0 g. (0.024 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (89% pure by g.l.c.) and 2.65 g. (0.0121 mole) of hexamethylcyclotrisilazane were heated at 175° for 48 hr. When the portion of the residue that was soluble in 10 ml. of petroleum ether, b.p. 60-90°, was distilled in a short-path apparatus, 6.3 g. (59% recovery) of distillate was collected between 108° (6 mm.) and 181° (0.03 mm.). There was 2.9 g. of residue. G.l.c. analyses of the distillate are reported as experiment No. 2 in Table I.

In a third experiment, a mixture of 7.6 g. (0.0230 mole) of N,N'-bis-(chlorodimethylsilyl)tetramethylcyclodisilazane (99% pure by g.l.c.) and 1.7 g. (0.0076 mole) of hexamethylcyclotrisilazane was heated at 175° for 48 hr., and then the portion of the residue soluble in 20 ml. of petroleum ether, b.p. 60-90°, was added to a solution of 10 ml. of dimethylamine in 10 ml. of petroleum ether, which was cooled in an isopropyl alcohol-Dry Ice bath. After the salts were filtered off and the filtrate was concentrated, distillation in a short-path apparatus gave 6.4 g. (69% recovery) of a distillate boiling between 100-220° (0.3 mm.) and 1.1 g. of a residue. G.l.c. analysis of the distillate is reported as experiment No. 3 in Table I.

TABLE I

G.L.C. ANALYSES OF THE EQUILIBRATION PRODUCTS OF N,N'-BIS(CHLORODIMETHYLSILYL)-TETRAMETHYLCYCLODISILAZANE AND HEXAMETHYLCYCLOTRISILAZANE

Experiment No.	Equilibration Conditions	Work-Up Procedure	Recovery of Materials (%)	G.l.c. Analyses[a] Peaks (percentage of peak areas)	
				1[b]	2[c]
1	175° for 48 hr. (3:1 mole ratio)	Distilled Directly	75	80	17
2	175° for 48 hr. (2:1 mole ratio)	Same	59	82	14
3	175° for 48 hr. (3:1 mole ratio)	Treated with Dimethylamine	69	84	10
4	140° for 48 hr. (3:1 mole ratio)	Same	60	80	4
5	175° for 48 hr. (2:1 mole ratio)	Same	59	73	22

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a/ One-meter column packed with 5% SE-30 on 80/100 Chromport XXX, flow rate 50 ml/min of N_2, 150°.

b/ N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane or its dimethylamine derivative.

c/ N-(Chlorodimethylsilyl)-N'-(3-chlorotetramethyldisilazanyl)tetramethylcyclodisilazane or its dimethylamine derivative.

Experiments Nos. 4 and 5 in Table I followed the procedure of experiment No. 3. In experiment No. 4, 9.8 g. (0.0296 mole) of N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (99% pure by g.l.c.) and 2.15 g. (0.0099 mole) of hexamethylcyclotrisilazane, heated at 140° for 48 hr., gave 7.2 g. (60% recovery) of a liquid boiling between 80-190° (0.2 mm.). In experiment No. 5, 8.0 g. (0.0242 mole) of N,N'-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane (97% pure by g.l.c.) and 2.65 g. (0.0121 mole) of hexamethylcyclotrisilazane were heated at 175° for 48 hr., and 6.2 g. (59% recovery) of distillate was obtained between 100-215° (0.1 mm.).

4. *Equilibration of hexamethylcyclotrisilazane with dimethyldichlorosilane (1:2 mole ratio) at a maximum temperature of 225°*: After a mixture of 65.7 g. (0.30 mole) of hexamethylcyclotrisilazane and 77.4 g. (0.60 mole) of dichlorodimethylsilane was heated to 225° in 25 hr., 125 ml. of petroleum ether, b.p. 60-90°, was added, and the mixture was filtered to remove ammonium chloride. Vacuum distillation of the petroleum ether-soluble portion gave three fractions in the following boiling ranges: a, 55.9 g., b.p. 150-160° (45 mm.); b, 10 g., b.p. 100-112° (0.2 mm.); c, 11.1 g., b.p. 120-166° (0.10 mm.). Redistillation of fraction (c) afforded an additional three fractions: a', 1.5 g., b.p. 103-116° (0.02 mm.); b', 2.0 g., b.p. 116-144° (0.02 mm.); c', 3.6 g., b.p. 110-143° (0.02 mm.), and 2.0 g. of residue. The first two fractions were distilled through a 6-in. micro column packed with glass rings and the last fraction was distilled through the same column without packing. G.l.c. analyses indicated three to four components in fractions b' and c'.

5. *Equilibration of hexamethylcyclotrisilazane and dichlorodimethylsilane (1:1 mole ratio) at 260°*: After 43.8 g. (0.20 mole) of hexamethylcyclotrisilazane and 25.8 g. (0.20 mole) of dichlorodimethylsilane were heated to 260° over an 8.5-hr. period and cooled, the residue was dissolved in 125 ml. of petroleum ether, b.p. 60-90°, and quenched with 90 ml. of diethylamine in 100 ml. of petroleum ether. After the diethylamine hydrochloride was filtered off, the filtrate was fractionally distilled through an unpacked 15-cm. column. Fractions boiling in the following ranges were obtained: a, 7.2 g., b.p. 134-156° (12 mm.); b, 5.1 g., b.p. 156-162° (12 mm.); c, 8.0 g., b.p. 163-173° (12 mm.); d, 4.0 g., b.p., 174-190° (12 mm.); e, 8.9 g., b.p. 123-152° (0.1 mm.); f, 4.7 g., b.p. 152-176° (0.1 mm.); g, 3.9 g., b.p. 178-200° (0.1 mm.); h, 4.7 g., b.p. 206-242° (0.1 mm.); and 6.5 g. of residue. When fractions a, b, c, and d were combined and redistilled through the same unpacked column, the following fractions were obtained: a', 10.0 g., b.p., 122-146° (12 mm.); b', 9.0 g., b.p. 146-161° (12 mm.); c', 2.2 g., b.p. 163-172° (12 mm.); and 3.0 g. residue. Redistillation of e, f, and the 3.0 g. residue from previous distillation through the same column gave two fractions: d', 5.0 g., b.p., 106-120° (0.1 mm.); e', 6.7 g., b.p. 130-152° (0.05 mm.); and

3.5 g. of residue. Combination and fractional short-path distillation of the 3.5 g. residue and fractions g and h gave the following fractions: f', 2.8 g., b.p. 179-186° (0.07 mm.); g', 4.6 g., b.p. 186-203° (0.07 mm.); and 4.0 g. of residue. G.l.c. analyses are reported in Table II.

TABLE II

G.L.C.[a] OF AN EQUILIBRATION REACTION QUENCHED WITH DIETHYLAMINE

Fraction	Boiling Range (°C)	Wt. (g.)	Peak No. and Area Percentage 1	2	3	4[b]	5[c]	6[d]	7	8
b'	146-161 (12 mm.)	9.0	Trace	Trace	20	38	35	7	-	-
d'	106-120 (0.1 mm.)	5.0	3	2	14	45	25	7	3	-
e'	130-152 (0.05 mm.)	3.5	4	-	2	17	31	31	15	-
f'	179-186 (0.07 mm.)	2.8	11	-	-	2	7	30	37	12
g'	186-203 (0.07 mm.)	4.0	6	-	-	-	3	27	42	21

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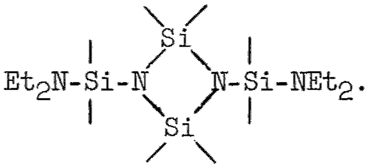
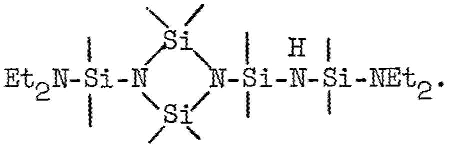
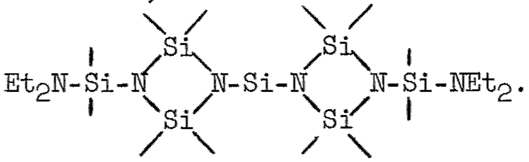
a/ One-meter column packed with 5% SE-30 on 80/100 Chromport XXX, 230°, flow rate 80 ml/min of N_2.

b/


c/


d/


G. Metallation of Silazanes

1. Sodium bis(trimethylsilyl)amide: Hexamethyldisilazane, 35.4 g. (0.22 mole) dissolved in 40 ml. of benzene, was added dropwise over a period of 0.5 hr. to a stirred solution of 7.8 g. (0.20 mole) of sodium amide in 70 ml. of benzene at room temperature. The mixture was stirred for 0.5 hr. at room temperature and then refluxed for 13 hr., filtered, and the filtrate was evaporated to obtain 27.4 g. (75%) of sodium bis(trimethylsilylamide which melted at 172-174° in a sealed capillary tube (reported, m.p. 165-167°) (Ref. 4).

2. N-Sodiohexamethylcyclotrisilazane: To 5.1 g. (0.22 g-atom) of sodium in 100 ml. of refluxing dioxane was added a solution of 43.8 g. (0.20 mole) of hexamethylcyclotrisilazane in 30 ml. (excess) of freshly distilled styrene in 0.75 hr. The mixture was heated for 2 hr., and then it was cooled and stored under nitrogen overnight. After the solution was decanted under nitrogen from a small amount of insoluble material, most of the dioxane was distilled off and 80 ml. of benzene was added to dissolve the solid material. The sodium salt, which precipitated when the solution was added to 250 ml. of petroleum ether, b.p. 60-90°, weighed 28.3 g. after it was washed 3 times with 60-ml. portions of petroleum ether. When the solid was heated under nitrogen from 100 to 200° in 1 hr. and at 200° for 1 hr., 3.5 g. of volatile material (mostly dioxane with some hexamethylcyclotrisilazane, identified by infrared spectrum) and 23.5 g. (49%) of N-sodiohexamethylcyclotrisilazane were obtained.

The N-sodiohexamethylcyclotrisilazane was characterized as follows: To a solution of 23.5 g. (0.0975 mole) of N-sodiohexamethylcyclotrisilazane in 50 ml. of 1,4-dioxane (distilled for sodium) was added 11.6 g. (0.106 mole) of chlorotrimethylsilane in 0.25 hr. while the temperature of the mixture was maintained at 30-35° with the occasional use of an ice bath. After the mixture was heated at reflux for 3 hr., it was cooled, filtered, and the solvent was distilled. Distillation of the residue gave 5.1 g. of hexamethylcyclotrisilazane, b.p. 79-86° (9 mm.), n_D^{20} 1.4432 and 12.9 g. (46% yield, 61% conversion) of hexamethyl-N-trimethylsilylcyclotrisilazane, b.p. 110-113° (9 mm.), n_D^{20} 1.4605 [reported, b.p. 111-112° (10 mm.), n_D^{20} 1.4596] (Ref. 17).

By an alternate procedure a mixture of 1.95 g. (0.050 mole) of sodium amide, 10.05 g. (0.055 mole) of hexamethylcyclotrisilazane, and 30 ml. of benzene was heated at reflux for 6 hr. The mixture, filtered hot under nitrogen, gave 8.1 g. (67%) of N-sodiohexamethylcyclotrisilazane, vacuum dried 7 hr. at 0.1 mm., 26°. After the solvent was evaporated from the filtrate, there remained about 3 g. of liquid residue. The infrared spectrum of the product is reported in Figure 31.

The sodium salt was characterized as follows: N-sodiohexamethylcyclotrisilazane, 8.1 g. (0.033 mole), was suspended in 100 ml. of petroleum ether, b.p. 60-90°, and stirred vigorously while 3.6 g. (0.033 mole) of chlorotrimethylsilane was added dropwise over a 4-hr. period. The mixture was then refluxed for 3 hr., stored overnight at room temperature, and filtered to remove 1.9 g. (calcd., 1.9 g.) of sodium chloride. The filtrate was concentrated on a rotary evaporator and vacuum distilled to give 3.0 g. (20%) of hexamethyl-N-(trimethylsilyl)cyclotrisilazane, b.p. 111-113° (9 mm.), n_D^{20} 1.4603.

3. Hexamethyl-N-sodio-N'-(trimethylsilyl)cyclotrisilazane: When a mixture of 17.5 g. (0.060 mole) of hexamethyl-N-(trimethylsilyl)cyclotrisilazane, 2.3 g. (0.060 mole) of sodium amide, and 20 ml. of benzene was heated at reflux for 6 hr., ammonia evolution was observed. After the solution was allowed to stand at room temperature for 7 days, large, colorless crystals formed. The mixture was warmed to redissolve the precipitate and filtered under nitrogen to remove a small amount of benzene-insoluble material. The filtrate was then allowed to stand for several days at room temperature as large hexagonal crystals formed. After the solution was decanted from the crystals and the crystals dried under reduced pressure, the infrared spectrum, Figure 32, of the residue showed no evidence for cyclodisilazane formation.

H. Condensation Polymers from Arylenedisilanols and Cyclodisilazane Derivatives

1. Bis(p-hydroxydimethylsilylphenyl) ether: The purity of the monomer that was prepared in May 1968 and was still being used for polymerizations in May 1969 was rechecked. The melting, 104-105°, had not changed and the infrared spectrum showed no significant development of siloxane absorption.

2. Preliminary experiments on polymers from bis(p-hydroxydimethylsilylphenyl) ether and N,N'-bis[(dialkylamino)dimethylsilyl]tetramethylcyclodisilazanes:

a. Condensates of bis(p-hydroxydimethylsilylphenyl) ether and N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane: The effect of solvent dilution in solution polymerizations was examined. A solution of 0.7962 g. (0.002500 mole) of bis(p-hydroxydimethylsilylphenyl) ether, 0.8720 g. (0.002500 mole) of N,N'-bis[(dimethylamino)dimethylsilyl]-tetramethylcyclodisilazane, and 10 ml. of toluene was heated at reflux for 7.5 hr. When the solvent was distilled off under reduced pressure the residue, the viscous liquid, had an inherent viscosity (0.5% in toluene at 30°) of 0.15 dl/g. Experiments at various dilutions are reported in Table III.

In a second series in which the millability of the polymers was examined, a mixture of 0.7962 g. (0.002500 mole) of bis(p-hydroxydimethylsilyl)phenyl ether, 0.8720 g. (0.002500 mole) of N,N'-bis[(dimethylamino)-dimethylsilyl]tetramethylcyclodisilazane, and 10 ml. of toluene was stirred at 27° under a nitrogen atmosphere, with a magnetic stirrer until the diol dissolved (1 hr.), and then 1 hr. longer. After the solvent was evaporated and the residue was heated at 90° for 2 hr., the polymer was examined for its millability with a threaded rod-cylinder apparatus. The results of this experiment and others with different amounts of solvents and different stirring times are reported in Table IV.

TABLE III

PRELIMINARY EXPERIMENTS ON THE POLYMERIZATION OF BIS(p-HYDROXYDIMETHYLSILYLPHENYL) ETHER[a] AND N,N'-BIS [(DIMETHYLAMINO)DIMETHYSILYL]-TETRAMETHYLCYCLODISILAZANE[b] IN TOLUENE

Experiment No.	Toluene (ml.)	Reflux Time (hr.)	Inherent Viscosity, 0.5% in Toluene, 30° (dl/g)	Nature of Polymer
1	5	0.66[c]	(58% Soluble)	Gel
2	10	7.5	0.15	Gum[d]
3	20	7.0	0.13	Gum[e]

---

[a] 0.7965 g. (0.00250 mole).

[b] 0.8723 g. (0.00250 mole).

[c] The polymer gelled.

[d] After 22 days the polymer had an inherent viscosity of 0.14 dl/g but the viscosity increased to 0.30 dl/g when the polymer was heated at 150° for 2 hr.

[e] After 17 days the polymer had an inherent viscosity of 0.30 dl/g.

TABLE IV

PRELIMINARY EXPERIMENTS ON THE CONDENSATION OF BIS(p- HYDROXYDIMETHYLSILYLPHENYL) ETHER AND N,N'-BIS[(DIMETHYLAMINO)DIMETHYLSILYL]TETRAMETHYLCYCLODISILAZANE UNDER VARIOUS MIXING CONDITIONS

Experiment No.	Volume Toluene (ml.)	Stirring Time (hr.)		Polymer Description	
		Before Monomers Dissolved	After Monomers Dissolved	Solubility in Toluene	Still Millable After (days)
1	10	1	1	Soluble[a]	36
2	10	1	3	Not completely soluble[b]	35
3	30	2.25	1	Not completely soluble[b]	34
4	30	2.5	3	Soluble[b]	33

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[a] Viscous fluid, not millable.
[b] Tacky gum, millable.

b. *Milling and curing studies*: In this series 1.5925 g. (0.005000 mole) of bis(*p*-hydroxydimethylsilylphenyl) ether and 1.7440 g. (0.005000 mole) of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane] or 2.0245 g. (0.005000 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane] in 20 ml. of toluene were mixed in a rotary evaporator at 35° until solid diol was no longer present (about 1 hr. for the dimethylamino derivative and about 2 hr. for the diethylamino derivative) and then one additional hour. After the solvent was distilled off at 35°, the residue was heated in a 60° bath for 2 hr. A 0.5 g. sample of the polymer was milled with 0.1 g. (20%) Cab-O-Sil in a threaded rod-cylinder apparatus. Polymers that crumbled were considered not millable. Additional samples were milled at suitable time intervals until they were no longer millable. The results of eight experiments are shown in Table V.

The milling apparatus consisted of a variable-speed stirrer (Gerald K. Heller Company, GT 21 Laboratory Mixer) with an aluminum rod (6 in. x 1/2 in., lower 1 in. threaded with 14 threads per inch) connected to the slow-speed stirrer shaft, and a stainless steel container (2-3/4 in. x 9/16 in. i.d., 10-ml. capacity). Polymer and some filler were placed into the container, and the container (handheld) was positioned under the rod. The stirrer was started at slow speed, and the container was raised until the threaded portion of the rod came in contact with the polymer. Slight pressure was applied so as to maintain contact, but not enough to overload the stirrer motor. The remaining filler was added to the container slowly. A stirring time of 2-5 min. was generally enough to obtain good mixing of the polymer and filler. Polymers that had a consistency similar to a conventional silicone gum milled easily, but polymers that were cross-linked enough to appear rubbery became crumbly.

In a first curing experiment, 1 g. of a polymer from N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(*p*-dimethylhydroxysilylphenyl) ether (η_{inh} = 0.11 dl/g) and 0.2 g. (20%) of Cab-O-Sil M-5 was milled and divided in half. About 0.005 g. of dicumyl peroxide was mixed into one sample. After 1 hr. at 150°, the sample containing curing agent was partially cured, but slightly tacky, and after 22 hr. at 150°, the treated sample was still slightly tacky. The untreated sample remained tacky.

When 1 g. of a polymer from N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(*p*-hydroxydimethylsilylphenyl) ether with an initial η_{inh} = 0.36 dl/g, but which had lost its solubility, was milled with 0.2 g. (20%) of Cab-O-Sil M-5 and divided in half, one portion was mixed with about 0.005 g. of dicumyl peroxide. After 1 hr. at 150°, the treated sample was rubbery, and the untreated sample was still soft.

TABLE V

PRELIMINARY EXPERIMENTS ON THE MILLING OF POLYMERS FROM BIS(p-DIMETHYLHYDROXYSILYL)PHENYL ETHER AND N,N'-BIS[(DIALKYLAMINO)DIMETHYLSILYL] TETRAMETHYLCYCLODISILAZANE

Experiment No.	R in Dialkylamino Group	Polymerization Temp. (°C)	Polymers Description and Yield (%)		Millable Initially	Age of Polymer when not Millable (days)
1	CH_3	60	Gum	97	Yes	5
2	C_2H_5	60	Fluid	124	No[a]	-
3	CH_3	90	Rubber	117	No	-
4	C_2H_5	90	Fluid	124	No[a]	-
5	CH_3	120	Gum	111	Yes	9
6	C_2H_5	120	Rubber	103	No	-
7	CH_3	150	Rubber	114	No	-
8	C_2H_5	150	Rubber	110	No	-

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[a] The polymer was a fluid that progressively became more viscous on standing. However, both were too fluid to mill after 16 days.

c. Endcapping experiments of polymers from N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane with bis(trimethylsilyl)-acetamide: A mixture of 1.5925 g. (0.005000 mole) of bis(p-hydroxydimethylsilylphenyl) ether, 1.7440 g. (0.005000 mole) of N,N'-bis[(dimethylamino)-dimethylsilyl]tetramethylcyclodisilazane, and 20 ml. of toluene was mixed in a rotary evaporator at 35° for 2 hr. After the solvent was distilled under reduced pressure, the residue was heated in a 60°-bath for 4 hr.

A portion of the polymer (1.5 g.) was dissolved in 10 ml. of a toluene solution containing 0.10 g. (0.00050 mole) of bis(trimethylsilyl)-acetamide, and the remaining polymer (1.9 g.) was dissolved in 10 ml. of toluene only. After both solutions were refluxed 2 hr., the solvent was distilled under reduced pressure and the polymers were heated in a 150°-bath for 2 hr. The untreated polymer gelled and formed a rubber in 1 hr. The treated polymer remained a gum that was soluble in toluene and had an inherent viscosity (0.5% in toluene at 30°) of 0.21 dl/g. Acetamide-containing impurities were removed when the polymer was dissolved in petroleum ether, b.p. 60-90°, washed once with water, the organic phase dried over Drierite, and the solvent was evaporated. The residue, a gum, had an inherent viscosity (0.5% in toluene at 30°) of 0.19 dl/g. Infrared spectra of the polymers before and after they were washed with water are shown in Figures 33 and 34. After 29 days, the polymer had an inherent viscosity of 0.22 dl/g.

Half of another polymer sample, similarly treated, gave an endcapped polymer with an inherent viscosity of 0.23 dl/g after it was heated at 150° for 2 hr. The other half of the polymer sample became crosslinked when it was heated at 150° for 1 hr.

In a series of experiments, 0.8722 g. (0.002500 mole) of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane and 0.7964 g. (0.002500 mole) of bis(p-hydroxydimethylsilylphenyl) ether were mixed in 10 ml. of toluene at 35° in a rotary evaporator for 2 hr. The toluene in experiments 1 and 2 (Table VI) was removed under reduced pressure at a maximum bath temperature of 40°. In the remaining experiments, the toluene solution was refluxed for the specified period, then removed under reduced pressure. After the polymeric residues were dissolved in toluene solution containing 0.010 g/ml of bis(trimethylsilyl)acetamide and refluxed for 2 hr., the toluene was removed under reduced pressure and the residue was heated for 2 hr. at 150°. Unless otherwise specified, all heating steps employed a heating mantle. The infrared spectra of the polymers that gelled did not differ significantly from the polymers that remained soluble. The polymer in experiment No. 5 was water-washed to remove acetamide-containing impurities in the following way: The polymer, 1.5 g., η_{inh} = 0.26 dl/g, was dissolved in 20 ml. of the toluene and washed once with 50 ml. of water. The toluene layer was subsequently dried over sodium sulfate and evaporated

TABLE VI

PRELIMINARY ENDCAPPING OF N,N'-BIS[(DIMETHYLAMINO)DIMETHYLSILYL]TETRAMETHYLCYCLODISILAZANE BIS(*p*-HYDROXYDIMETHYLSILYLPHENYL) ETHER CONDENSATES WITH N,N'-BIS(TRIMETHYLSILYL)ACETAMIDE

Initial Solution Polymerization			Endcapping Step			Final Polymerization Step, 2 hr. at 150°	
Experiment No.	Heating Time (hr.)	η inh (dl/g)	Bis(trimethylsilyl)-acetamide Solution (ml.)	Toluene (ml.)	η inh (dl/g)	η inh (dl/g)	Nature of the Polymer
1	not heated	0.06	2.5	7.5	--	34% soluble	--
2	not heated	0.08	3.75	6.25	--	49% soluble	--
3	4	0.09	2.5	7.5	--	0.51	gum
4	4	0.08	1.25	8.75	0.10	54% soluble	gum
5	8	0.10	2.5	7.5	0.09	0.26 (0.30)[a]	gum
6	8	0.08	2.0	8.0	0.09	0.30	gum
7	8	gelled	2.5[b]	--	--	--	--
8	8	gelled	2.5[b]	--	--	--	--
9	2	0.08	5.0	5.0	--	0.17	gum
10	2[c]	0.14	2.5	--	0.16	0.35	gum

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[a] η inh after water wash.

[b] The bis(trimethylsilyl)acetamide solution was added directly to the product of the first step without removing the toluene.

[c] Heated on a steam bath at 99°.

to obtain a gum with an inherent viscosity of 0.30 dl/g. When polymer No. 9 was heated for an additional 2 hr. at 150°, the inherent viscosity increased from 0.17 to 0.21 dl/g. The solubility characteristics of polymer No. 3 had not changed after 20 days' storage.

d. Preliminary experiments on polymers from N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(p-hydroxydimethylsilylphenyl) ether: In a typical experiment for the polymers reported in Table VII, a solution of 1.0123 g. (0.0025 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and 0.7962 g. (0.002500 mole) of bis(p-dimethylhydroxysilylphenyl) ether in 10 ml. of toluene were stirred 2 hr. at room temperature and then heated for 2 hr. on a steam bath. After the solvent was distilled in a rotary evaporator, the residue was heated at 150° for 2 hr. under nitrogen in a Wood's metal bath. The inherent viscosity increased from 0.08 to 0.41 dl/g. The polymer in 8.8 ml. of toluene and 1.2 ml. of a solution of 0.01 g/ml of bis(trimethylsilyl)acetamide in toluene was again heated for 2 hr. on a steam bath. After the solvent was removed under reduced pressure at 50°, the residue was heated at 150° in a Wood's metal bath under nitrogen in most experiments, but the step was omitted in this one and several others. The polymer was then dissolved in 30 ml. of petroleum ether, b.p. 60-90°, washed with 50 ml. of water, dried over sodium sulfate, the petroleum ether was removed under reduced pressure, and the residue heated in a mantle under reduced pressure to 150°. Its inherent viscosity was 0.80 dl/g, but the polymer lost its solubility after 7 days.

After the polymers were stored for various periods of time, a sample from each of experiments 1, 3, 11, 13, and 15 was heated at 200° for 2 hr. in a Wood's metal bath. Samples 3 and 11 lost solubility. The others remained soluble and had the following inherent viscosities after the heating period: No. 1, 0.35; No. 13, 0.45; and No. 15, 0.56 dl/g.

3. Preparation of endcapped samples of condensates of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane with bis(p-hydroxydimethylsilylphenyl) ether: The following is the method of preparation for the samples described in Table VIII. After a mixture of 0.8722 g. (0.002500 mole) of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane, 0.7974 g. (0.002500 mole) of bis(p-hydroxydimethylsilylphenyl) ether, and 10 ml. of toluene were mixed on a rotary evaporator until the monomers dissolved, the toluene solution was heated on a steam bath for 2 hr. After 2.5 ml. of a 0.010 g/ml solution of bis(trimethylsilyl)acetamide in toluene was added, the solution was heated for an additional 2 hr. on the steam bath. When the solvent was removed under reduced pressure, the residue had an inherent viscosity of 0.15 dl/g. The inherent viscosity increased to 0.24 dl/g after the residue was heated at 150° for 2 hr. in a Wood's metal bath. When the polymer was dissolved in 20 ml. of petroleum

TABLE VII

SYNTHESIS OF ENDCAPPED CONDENSATES OF N,N'-BIS[(DIETHYLAMINO)DIMETHYLSILYL]TETRAMETHYLCYCLODISILAZANE AND BIS(p-HYDROXYDIMETHYLSILYL)PHENYL ETHER

Initial Polymerization Step Solution Polymerization			Heating Period		Endcapping Step			Final Polymerization			After Water Wash	After Storage	
Experiment No.	(Time and Temperature)	η_{inh} (dl/g)	(Time and Temperature)	η_{inh} (dl/g)	Bis(trimethylsilyl)-acetamide Solution (ml.)	Toluene (ml.)	η_{inh} (dl/g)	Time and (hr.)	Temperature (°C)	η_{inh} (dl/g)	η_{inh} (dl/g)	Days	η_{inh} (dl/g)
1.	In toluene on steam bath for 2 hr.	0.05	None	--	2.5	7.5	0.09	2	150	0.26	0.28	32 41	0.30 0.35[a]
2.	In toluene on steam bath for 2 hr.	0.06	None	--	1.5	8.5	0.10	2	150	0.36	0.57	31	0.73
3.	In toluene on steam bath for 2 hr.	--	None	--	1.0	10.0	0.10	2	150	0.35	0.58	29 39	0.77 Solubility Loss[a]
4.	In toluene on steam bath for 2 hr.	--	None	--	0.5	10.0	0.08	2	150	0.31	0.43	25	0.52
5.	In toluene on steam bath for 2 hr.	0.08	2 hr. at 150°	0.41	1.2	13.8	0.35	None		--	0.80	7	Solubility Loss
6.	In refluxing toluene for 2 hr.[b]	0.10	None	--	1.2	8.8	0.12	2	150	--	0.52	23	0.57
7.	In refluxing xylene for 2 hr.[b]	--	80° for 15 min.[c]	0.23	1.2	8.8	0.17	2	150	--	0.28	--	--
8.	In toluene on steam bath for 2 hr.	--	None	--	1.2	8.8	0.15	2	150	0.15	0.48	22	0.81
9.	In toluene on steam bath for 2 hr.	--	2 hr. at 100°	0.15	1.2	8.8	0.15	None		--	0.40	16	0.45
10.	In refluxing toluene on a sand bath for 2 hr.	--	2 hr. at 100°	0.28	1.2	8.8	0.26	2	150[c]	0.62	Lost solubility after 3 days		
11.	In refluxing xylene on a sand bath for 2 hr.	--	2 hr. at 100°	0.19	1.2	8.8	0.17	2	150[c]	0.52	0.70[c]	12 18	0.70 Solubility Loss[a]
12.	In toluene on a steam bath for 2 hr.	--	2 hr. at 100°	0.46	1.2	8.8	0.36	2	150[c]	0.70	0.67[c]	12	0.67
13.	In toluene on a steam bath for 2 hr.	--	2 hr. at 100°	--	2.0	8.0	--	2	150[c]	0.38	0.38[c]	5	0.45[a]
14.	In toluene on a steam bath for 2 hr.	--	2 hr. at 100°	--	2.5	7.5	--	2	150[c]	0.64	0.69[c]		
15.	In toluene on a steam bath for 2 hr.	--	2 hr. at 100°	--	3.0	7.0	--	2	150[c]	0.41	0.41[c]	5	0.56[a]

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[a] After 200° the polymer was heated for 2 hr. under vacuum in a Wood's metal bath; [b] Heated on a sand bath; [c] Under vacuum; [d] Heated in a Wood's metal bath.

TABLE VIII

SYNTHESIS OF ENDCAPPED CONDENSATES OF N,N'-BIS[(DIMETHYLAMINO)DIMETHYLSILYL]TETRAMETHYLCYCLODISILAZANE WITH BIS(p-HYDROXYDIMETHYLSILYLPHENYL) ETHER

Initial Solution Polymerization			Endcapping Step			Final Polymerization Step, 2 hr. at 150°		
Expt. No.	Molar Quantities	Heating Time (hr.)	Bis(trimethylsilyl)-acetamide Solution (ml.)	Toluene (ml.)	η_{inh} (dl/g)	η_{inh} (dl/g)	Yield (%)	Nature of the Polymer
1.	0.0025	2	2.5	--	0.15	0.24 (0.30)[a]	--	gum
2.	0.00750	2	7.5	--	0.30	0.41 (0.70)[a]	72	gum
3.	0.02250	2	22.5	--	0.26	0.28 (0.34)[a]	95	gum
4.	0.05475	2	52.5	--	--	0.24 (0.26)[a]	96	gum

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[a] η_{inh} after water wash.

ether, b.p. 60-90°, washed with 50 ml. of water, dried over sodium sulfate, and the petroleum ether was removed under reduced pressure, the final polymer had an inherent viscosity of 0.30 dl/g. In the polymerizations that used larger quantities of monomers, proportionately larger quantities of reagents and solvents were also used. Polymer No. 1, heated 2 hr. at 150°, showed an increase in the inherent viscosity of from 0.30 to 0.33 dl/g, but an additional 4-hr. heating did not change the viscosity. The infrared spectrum for polymer No. 4 is reported in Figure 35. The following elemental analysis was obtained for polymer No. 4:

Anal. Calcd. for $C_{24}H_{44}N_2O_3Si_6$: C, 49.94; H, 7.68; N, 4.85; Si, 29.20. Found: C, 49.83; H, 7.76; N, 4.69; Si, 29.31.

4. Preparation of endcapped samples of condensates of N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(p-hydroxydimethylsilylphenyl) ether:

a. Sample with a low level of bis(trimethylsilyl)acetamide: A solution of 8.0984 g. (0.02000 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and 6.3696 g. (0.02000 mole) of bis(p-hydroxydimethylsilylphenyl) ether in 80 ml. of toluene was stirred for 2 hr. at room temperature and then heated for 2 hr. on a steam bath. After the solvent was distilled in a rotary evaporator, the inherent viscosity of the residue was 0.06 dl/g. The residue, dissolved in 70.4 ml. of toluene and 9.6 ml. of a solution of 0.010 g/ml of bis(trimethylsilyl)acetamide in toluene, was heated for 2 hr. on a steam bath. After the solvent was removed under reduced pressure at 50°, the inherent viscosity of the residue was 0.10 dl/g. When the polymer was heated at 150° for 2 hr. under nitrogen in a Wood's metal bath, the inherent viscosity of the polymer increased to 0.60 dl/g. The polymer was then dissolved in 240 ml. of petroleum ether, b.p. 60-90°, washed with 400 ml. of water, dried over anhydrous sodium sulfate and the petroleum ether was removed under reduced pressure. The residue was heated in a mantle under reduced pressure to 150° to afford 9.7119 g. (81%) of polymer, T_g -20°; infrared spectrum, Figure 36; η_{inh} 0.80 dl/g. The polymer became only partially soluble on standing for 11 days at room temperature.

Anal. Calcd. for $C_{24}H_{44}N_2O_3Si_6$: C, 49.99; H, 7.69; N, 4.86; Si, 29.14. Found: C, 50.29; H, 7.63; N, 4.88; Si, 29.75.

Immediately after its preparation, a 0.25-g. sample of the polymer was heated at 200°, under nitrogen, for 2 hr. and a 0.1-g. portion placed in 20 ml. of toluene. After being shaken for 12 hr., the polymer swelled and was only 60% soluble in toluene. When the swollen, insoluble portion was filtered off, the inherent viscosity of the soluble portion was 1.00 dl/g (after correction for the concentration in solution).

b. Samples with a high level of bis(trimethylsilyl)acetamide: Subsequently, five polymer samples (Table IX) were prepared in the following manner. A solution of 8.0984 g. (0.02000 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and 6.3696 g. (0.02000 mole) of bis(p-hydroxydimethylsilylphenyl) ether in 80 ml. of toluene was stirred for 2 hr. at room temperature and then heated for 2 hr. on a steam bath under nitrogen. After the solvent was distilled in a rotary evaporator, the residue was heated at 100° for 2 hr. under vacuum in a Wood's metal bath. The polymer was then dissolved in 64 ml. of toluene and 20 ml. of a solution of 0.01 g/ml of bis(trimethylsilyl)acetamide in toluene and heated for 2 hr. on a steam bath under nitrogen. After the solvent was removed under reduced pressure at 50° and the residue heated at 150° for 2 hr. under vacuum in a Wood's metal bath, the endcapped polymer was dissolved in 120 ml. of petroleum ether, b.p. 60-90°, washed with 250 ml. of water, dried over anhydrous sodium sulfate, and the petroleum ether was removed under reduced pressure at 50°. The polymer was finally heated at 150° for 15 min. under reduced pressure. The inherent viscosities of the polymers were determined at various stages in the polymerization, during storage, and after heating a 0.20-g. sample at 200° under a vacuum.

c. Endcapped samples of gelled polymers: Three samples, that were advanced to different degrees of polymerization, were prepared as follows: A solution of 28.0596 g. (0.06930 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and 22.0734 g. (0.06930 mole) of bis(p-hydroxydimethylsilylphenyl) ether in 280 ml. of toluene was stirred for 2 hr. at room temperature and then heated for 2 hr. on a steam bath. After the solvent was distilled in a rotary evaporator, the residue was heated at 100° for 2 hr. under vacuum in a Wood's metal bath. The inherent viscosity of the polymer was 0.21 dl/g. A 10-g. sample was taken, heated at 150° for 2 hr. under vacuum in a Wood's metal bath, dissolved in 52 ml. of toluene, and endcapped by adding 17.4 ml. of a 0.01 g/ml solution of bis(trimethylsilyl)acetamide and heating the solution over steam for 2 hr. under nitrogen. The solvent was removed under reduced pressure at 50° and the residue heated at 150° for 2 hr. under vacuum in a Wood's metal bath. The sample was then dissolved in 100 ml. of petroleum ether, b.p. 60-90°, washed with 100 ml. of water, dried over anhydrous sodium sulfate, and the solvent distilled on a rotary evaporator. After the residue was heated at 200° for 15 min. under a vacuum in a Wood's metal bath, 8.27 g. (83%) of polymer was obtained (Sample No. 1) with an inherent viscosity of 0.89 dl/g.; infrared spectrum, Figure 37.

TABLE IX

INHERENT VISCOSITIES (dl/g) OF ENDCAPPED CONDENSATES OF N,N'-BIS[(DIETHYLAMINO)-DIMETHYLSILYL]TETRAMETHYLCYCLODISILAZANE AND BIS(p-HYDROXYDIMETHYLSILYL)PHENYL ETHER

Experiment No.	After 150° Heating	After Water Wash	After Storage		After 200° Heating of a 0.20 g. Sample	Percent Yield
			Days	η_{inh}		
1	0.10	0.10	-	-	-	-
2	0.64	0.67	8 11	0.64 0.62	0.88	73
3	0.36	0.39	9	0.43	0.69	97
4	0.40	0.46	5 9	0.49 0.48	0.60[a] 0.61[b]	103
5[c]	0.26	0.28			0.26[a]	

---

[a] Entire polymer sample heated to 200° under vacuum.

[b] Redetermined after 11 days of storage.

[c] The cyclodisilazane monomer in the preparation ultimately proved to be 94.2% pure.

The remaining 30 g. of material was heated for 2 hr. at 100° under vacuum in a Wood's metal bath to afford a polymer with an inherent viscosity of 0.24 dl/g. Additional heating of the polymer at 150° for 2 hr. increased the inherent viscosity to 0.92 dl/g. A 10-g. sample was removed and partially dissolved in 104 ml. of toluene (gel formation) and endcapped in the same manner as sample No. 1. The solvent was distilled at 50° under vacuum and the residue heated for 2 hr. under vacuum at 150° in a Wood's metal bath to give 9.98 g (100%) of a polymer (sample No. 2), infrared spectrum, Figure 38.

The remaining 20 g. of sample was heated for 2 hr. at 150° under vacuum in a Wood's metal bath, partially dissolved (gel formation) in 156 ml. of toluene, endcapped in the conventional manner, and the solvent removed by distillation to give 16.1 g. (81%) of polymer (sample No. 3) infrared spectrum, Figure 39.

5. Endcapping of a bis(p-hydroxydimethylsilylphenyl) ether - N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane condensate with dimethylphenylsilanol: In the following two experiments, similarly prepared polymers were endcapped, one with bis(trimethylsilyl)acetamide and the other with dimethylphenylsilanol. Solutions of 1.0126 g. (0.002501 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and 0.7965 g. (0.002501 mole) of bis(p-hydroxydimethylsilylphenyl) ether in 10 ml. of toluene were polymerized in the manner described in paragraph IV.H.4.b. Each polymer dissolved in 7.5 ml. of toluene was treated with 2.5 ml. (conc. 0.0100 g/ml) of the endcapping reagent indicated in Table IX. Inherent viscosities, determined at various stages in the polymerization, are reported in Table X.

TABLE X

INHERENT VISCOSITIES (dl/g) OF CONDENSATES OF N,N'-BIS[(DIETHYLAMINO)DIMETHYLSILYL]TETRAMETHYLCYCLODISILAZANE AND BIS(p-HYDROXYDIMETHYLSILYLPHENYL) ETHER ENDCAPPED WITH DIMETHYLPHENYLSILANOL AND BIS(TRIMETHYLSILYL)ACETAMIDE

Experiment No.	After 150° Heating	After Water Wash	After 200° Heating	Endcapping Reagent
1	0.30	0.35	1.11	Bis(trimethylsilyl)-acetamide
2	0.33	0.35	Insoluble	Dimethylphenylsilanol[a]

---

[a] Freshly distilled, b.p. 102-104°.

6. Polymerization of decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, *p*-phenylenebis(dimethylsilanol) and *p*-phenylenebis(methylvinylsilanol): A mixture of 3.226 g. (0.01000 mole) of decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, 2.1509 g. (0.00950 mole of *p*-phenylenebis(dimethylsilanol), and 0.1252 g. (0.000500 mole) of *p*-phenylenebis-(methylvinylsilanol) was heated at 160° for 4 hr. under nitrogen in a Wood's metal bath. The resulting polymer was cooled, dissolved in 40 ml. of toluene, washed with 40 ml. of water, and dried over anhydrous sodium sulfate. After the toluene was distilled on a rotary evaporator at 50°, 5.20 g. (96%) of a polymer with an inherent viscosity of 0.56 dl/g was obtained.

In a similar polymerization 32.269 g. (0.1000 mole) of decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, 21.509 g. (0.09500 mole) of *p*-phenylenebis(dimethylsilanol), and 1.252 g. (0.00500 mole of *p*-phenylenebis(methylvinylsilanol) gave 55.0 g. (100%) of a polymer with an inherent viscosity of 0.72 dl/g. Its infrared spectra is reported in Figure 40.

7. Polymerizations of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, bis(*p*-hydroxydimethylsilylphenyl) ether, and *p*-phenylenebis(methylvinylsilanol): In a series of experiments a solution of 1.0126 g. (0.002500 mole) of N,N'-bis[(diethylamino)dimethylsilyl]-tetramethylcyclodisilazane and the appropriate amounts of bis(*p*-hydroxydimethylsilylphenyl) ether and *p*-phenylenebis(methylvinylsilanol) (Table XI) in 10 ml. of toluene was polymerized by the method described in paragraph IV.H.4.b.

8. Polymerization of bis(*p*-dimethylhydroxysilylphenyl) ether and N,N'-bis[dimethyl(piperidino)silyl]tetramethylcyclodisilazane: After 2.1067 g. (0.004912 mole) of N,N'-bis[dimethyl(piperidino)silyl]tetramethylcyclodisilazane and 1.5645 g. (0.004912 mole) of bis-(*p*-hydroxydimethylsilylphenyl) ether were polymerized by the method described in paragraph IV.H.4.b., 2.3 g. (82% of a polymer with an inherent viscosity of 0.19 dl/g was obtained.

In a second experiment with 1.0723 g. (0.002500 mole) of N,N'-bis-[dimethyl(piperidino)silyl]tetramethylcyclodisilazane and 0.7965 g. (0.002500 mole) of bis(*p*-hydroxydimethylsilylphenyl) ether, the polymer had an inherent viscosity of 0.28 dl/g after the water washing step and 0.39 dl/g after it was heated for 2 hr. at 200° under vacuum.

9. Polymerization of *p*-phenylenebis(dimethylsilanol) and N,N'-bis[(dialkylamino)dimethylsilyl]tetramethylcyclodisilazanes: After 1.0123 g. (0.002500 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and 0.5660 g. (0.002500 mole) of *p*-phenylenebis-(dimethylsilanol) were polymerized in the manner described in paragraph IV.H.4.b., the following inherent viscosities were obtained: After the 150° heating, 0.19 dl/g; after water washing, 0.17 dl/g; and after the 200° heating, 0.26 dl/g.

TABLE XI

CONDENSATION POLYMERS FROM N,N'-BIS[(DIETHYLAMINO)DIMETHYLSILYL]TETRAMETHYLCYCLODISILAZANE WITH BIS(p-HYDROXYDIMETHYLSILYLPHENYL) ETHER AND p-PHENYLENEBIS(METHYLVINYLSILANOL) OR p-PHENYLENEBIS(DIMETHYLSILANOL)

Experiment No.	Bis(p-dimethylhydroxysilylphenyl) Ether (A) (g. mole)	p-Phenylenebis(methylvinylsilanol) (B) (g. mole)	p-Phenylenebis(dimethylsilanol) (C) (g. mole)	Mole % of B or C	Inherent Viscosity (dl/g) After 150° Heating
1	0.7883 (0.002475)	0.0063 (0.000025)	--	1.0	--[a]
2	0.7803 (0.002450)	0.0125 (0.000050)	--	2.0	0.89[b]
3	0.7724 (0.002425)	0.0188 (0.000075)	--	3.0	--[a]
4	0.7644 (0.002375)	0.0313 (0.000125)	--	5.0	0.56[c]
5	0.7644 (0.002375)	0.0312 (0.000125)	--	5.0	--[a,d]
6	0.7644 (0.002400)	--	0.0283 (0.000125)	5.0	0.36[c]

---

[a] Solubility loss occurred during the 150° heating.
[b] Solubility loss occurred before the water wash.
[c] Solubility loss occurred during the 200° heating.
[d] The inherent viscosity before the endcapping step was 0.30 dl/g.

When the procedure was repeated, the inherent viscosities at the three stages were 0.23, 0.31, and 0.38 dl/g, respectively.

An attempt to prepare a polymer from p-phenylenebis(dimethylsilanol) and N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane by the same procedure resulted in gelation after the 150° heating step. Omission of the 100° and the 150° heating steps with the same monomers gave a polymer with an inherent viscosity of 0.17 when the final heating temperature was 150°.

10. Condensation of polymers with excess bis(p-hydroxydimethylsilyl)-phenyl ether: A weighed amount of polymer, 0.4048 g., prepared by the condensation of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(p-dimethylhydroxysilylphenyl) ether, inherent viscosity 0.81 dl/g (0.5% concentration in toluene 30°), was dissolved in 20 ml. of toluene and 0.0080 g. (2 wt. %) of bis(p-hydroxydimethylsilylphenyl) ether was added. After the mixture was stirred until the diol dissolved (0.25 hr.), the solvent was distilled off on a rotary evaporator, and the residue was heated in a Wood's metal bath at 200° for 2 hr. under nitrogen. The residue had an inherent viscosity of 0.58 dl/g (0.5% in toluene, 30°). The results of this and additional experiments are shown in Table XIII.

TABLE XII

CONDENSATION OF POLYMERS WITH EXCESS BIS(p-HYDROXYDIMETHYLSILYL)PHENYL ETHER

Experiment No.	Initial Inherent η_{inh} (dl/g)	Diol (wt. %)	Final Inherent η_{inh} (dl/g)
1	0.81	2	0.58
2	0.81	5	0.38
3	0.26	0.5	0.28
4	0.26	1	0.28
5	0.41	1	0.58

11. Polymers from bis(p-hydroxydimethylsilylphenyl) ether and α,ω-dimethyldimethylaminosilyl oligomeric cyclodisilazanes:

a. The oligocyclodisilazane with two rings: A mixture of 0.6370 g. (0.002000 mole) of bis(p-hydroxydimethylsilylphenyl) ether and 1.1026 g. (0.002000 mole) of α,ω-dimethyldimethylaminosilyl oligomeric cyclodisilazane, the two-ring compound, in 10 ml. of toluene was rotated on a rotary evaporator at 40° for 2 hr. After the solvent was distilled off under reduced pressure, the residue was heated at 60° for 3.5 hr. and at 120° for 9.5 hr. The polymer, 1.7 g. (109%), was a gum with an inherent viscosity of 0.33 dl/g (0.5% in toluene at 30°). The infrared spectrum of the polymer is reported in Figure 41. The polymer was about 90% soluble in toluene after 75 days.

b. The oligocyclodisilazane with four rings: A mixture of 0.3185 g. (0.001000 mole) of bis(p-hydroxydimethylsilylphenyl) ether and 0.9563 g. (0.001000 mole) of α,ω-dimethyldimethylaminosilyl oligomeric cyclodisilazane, the four-ring compound, in 10 ml. of toluene was rotated in a rotary evaporator at 35° for 2 hr. After the solvent was evaporated and the residue was heated at 60° for 3.5 hr. and 90° for 8.5 hr., the residual gum had an inherent viscosity of 0.14 dl/g in toluene (0.5% at 30°). The infrared spectra are reported in Figure 42. The polymer remained toluene-soluble after 54 days.

12. Hydrolytic stability of N,N'-bis[(dialkylamino)dimethylsilyl]-tetramethylcyclodisilazane-bis(p-hydroxydimethylsilylphenyl) ether condensates and similar condensates from oligocyclodisilazanes: In the preliminary experimental work, a polymer, which was prepared from the diethylamino derivative of the cyclodisilazane and had an original inherent viscosity of 0.21 dl/g, was employed. A film of the polymer was cast from toluene solution onto a sodium chloride optic, which had been coated with paraffin wax on all its surfaces not coated with the polymer. When the coated optic was exposed at room temperature in a desiccator containing water, the polymer film, which remained intact, was loosened by moisture that penetrated the film and damaged the surface of the optic in as little as 4 hr.

In subsequent experiments, a "KRS-5" (thallium bromide-iodide, Harshaw Chemical Company) optic was used. The film was again cast from toluene solution, and infrared spectra were taken after specified exposures in the desiccator containing water. The polymer was not visibly affected after 22 hr., but observable changes had occurred after 48 hr. After 66 hr., the Si_2N frequency at 880 cm^{-1} and 1035 cm^{-1} was considerably weakened. The spectra taken after 0, 22, 48, and 66 hr. are shown in Figures 43, 44, 45, 46, respectively. Since some of the polymer was leached from the optic during the exposure, the intensity of the $SiCH_3$ band at 1255 cm^{-1} also decreased in intensity with time; therefore, changes in the intensity of the 880 cm^{-1} and the 1035 cm^{-1} were compared as the ratio of each band's intensity after a certain time with the original intensity of the 1255 cm^{-1} band. These data are illustrated in Figure 1.

Similar data were also obtained for condensation polymers obtained from the oligocyclodisilazanes, n = 2 and 4, whose preparations are described elsewhere in the report (see paragraphs IV.H.11.a and IV.H.11.b). These data are also shown in Figure 1.

A polymer with an initial inherent viscosity of 0.26 dl/g and a satisfactory elemental analysis (Table VIII, polymer No. 4), which had been prepared from N,N'-bis[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(p-hydroxydimethylsilylphenyl) ether and endcapped with bis(trimethylsilyl)acetamide, was similarly examined for its hydrolytic stability. These results are compared with the results for a similar study of a non-endcapped polymer reported in Figure 2.

In a first experiment with a somewhat thicker polymer film, no hydrolytic decomposition was observed until 120 hr. The experiment was probably somewhat less sensitive to the detection of a change owing to the relatively strong absorptions of the infrared bands.

13. Thermogravimetric analysis of an endcapped polymer: A trace for the dynamic thermogravimetric analysis for an endcapped polymer (Table VIII, polymer No. 4) is reproduced in Figure 3. Isothermal thermogravimetric analyses experiments were conducted on an Aminco thermogravimetric unit modified so that the isothermal furnace temperature was controlled by an external Powerstat and a West Controller. A 0.1016 g. sample of the same endcapped polymer was heated isothermally at 340° (± 1°) for 6.6 hr. The weight loss was 0.0080 g., or 7.9%. Additional isothermal traces were conducted at 260°, 300°, 380°, 420°, and 460°, and are shown in Figure 4.

REFERENCES

1. Fink, W., Helv. Chim. Acta, 51, 1743 (1968).

2. Geymayer, P., and E. G. Rochow, Angew, Chem. Internat. Ed., 4, 592 (1965).

3. Wannagat, U., and H. Niederpruem, Chem. Ber., 94, 1540 (1961).

4. Bush, R. P., and C. A. Pearce, J. Chem. Soc. (A), 808 (1969).

5. Rumba, G. Ya, and Ya. E. Rozhkaln, Latv. PSR Zinat. Akad. Vestis, Khim. Ser., No. 4, 507 (1968); C. A., 70, 28989 (1969).

6. Bailey, D. L., L. H. Sommer, and F. C. Whitmore, J. Amer. Chem. Soc., 70, 435 (1948).

7. Martin, G., and F. S. Kipping, J. Chem. Soc., 95, 308 (1909).

8. Dolgov, B. N., N. P. Kharitonov, and M. G. Voronkov., Zh. Obshch. Khim., 24, 678 (1954).

9. Dannley, R. L., and G. Jalics, J. Org. Chem., 30, 2717 (1965).

10. Fessenden, R. W., J. Org. Chem., 25, 2191 (1960).

11. Breed, L. W., and R. L. Elliott, J. Organometal. Chem., 9, 188 (1967).

12. Strober, M. R., K. W. Michael, and J. L. Speier, J. Org. Chem., 32, 2740 (1967).

13. Fink, W., Helv. Chim. Acta, 51, 1011 (1969).

14. Breed, L. W., W. L. Budde, and R. L. Elliott, J. Organometal. Chem., 6, 676 (1966).

15. Breed, L. W., and R. L. Elliott, J. Organometal. Chem., 11, 447 (1968).

16. Cohen, M., and J. R. Ladd, J. Amer. Chem. Soc., 75, 988 (1953).

17. Zhinkin, D. Ya., N. V. Markova, and M. V. Sobolevskii, Zh. Obshch. Khim., 33 (8), 2638-40 (1963); C. A., 60, 540d (1964).

18. Breed, L. W., and R. L. Elliott, Inorg. Chem., 2, 1069 (1963).

APPENDIX I

FIGURES 5 THROUGH 46, INFRARED SPECTRA

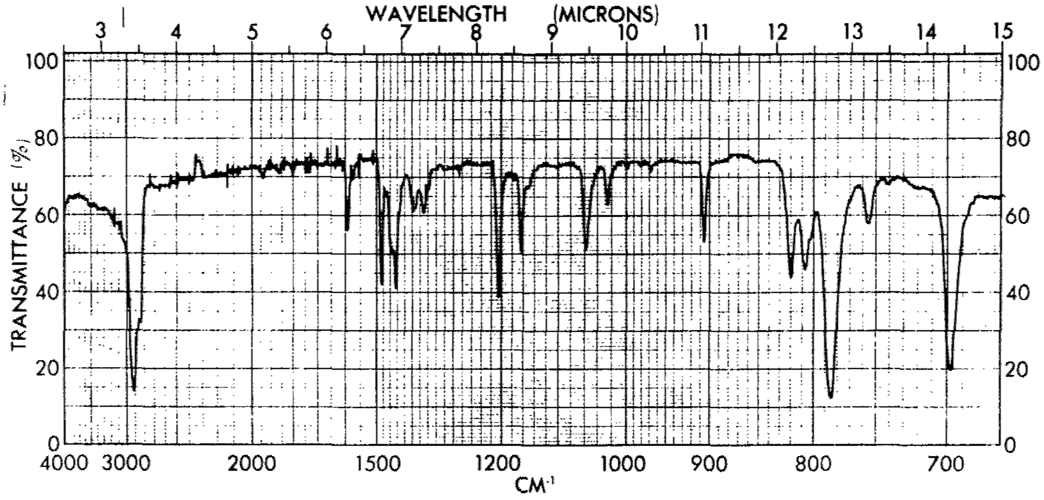

Figure 5 - Infrared Spectrum of Chlorotribenzylsilane (Nujol)

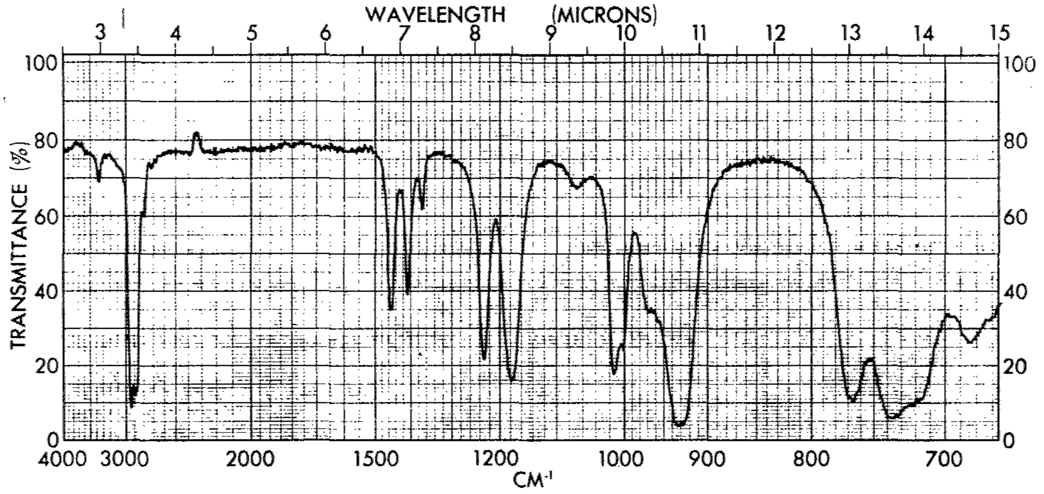

Figure 6 - Infrared Spectrum of Hexaethyldisilazane (Liquid)

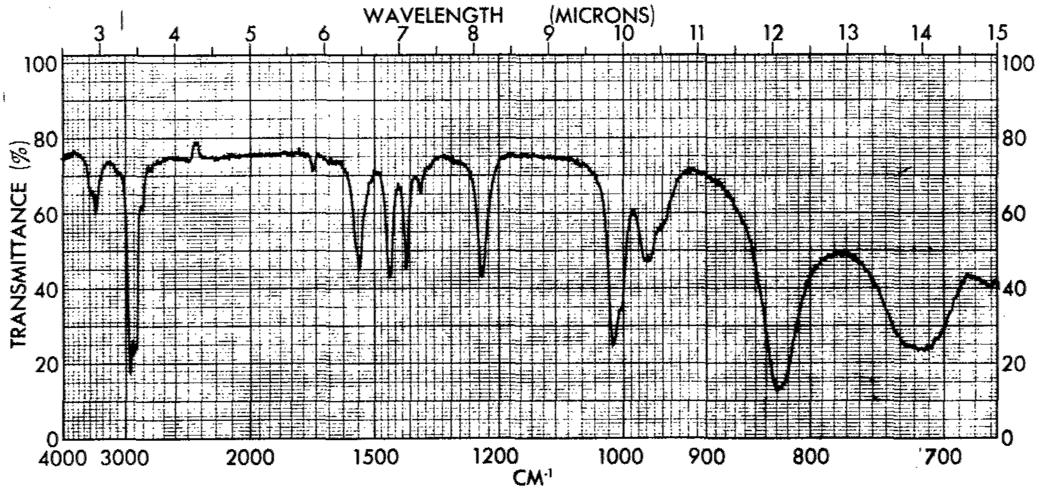

Figure 7 - Infrared Spectrum of Triethylsilylamine (Liquid)

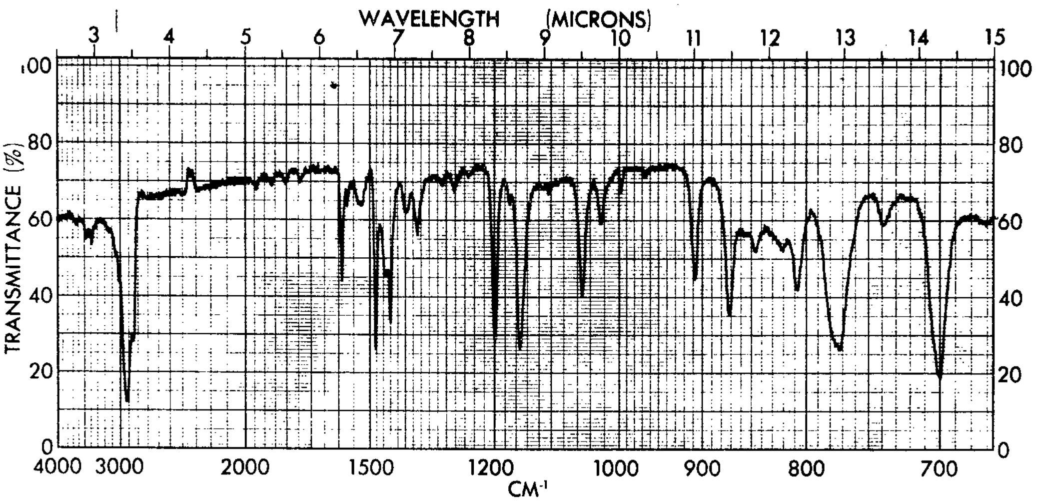

Figure 8 - Infrared Spectrum of Tribenzylsilylamine (Nujol)

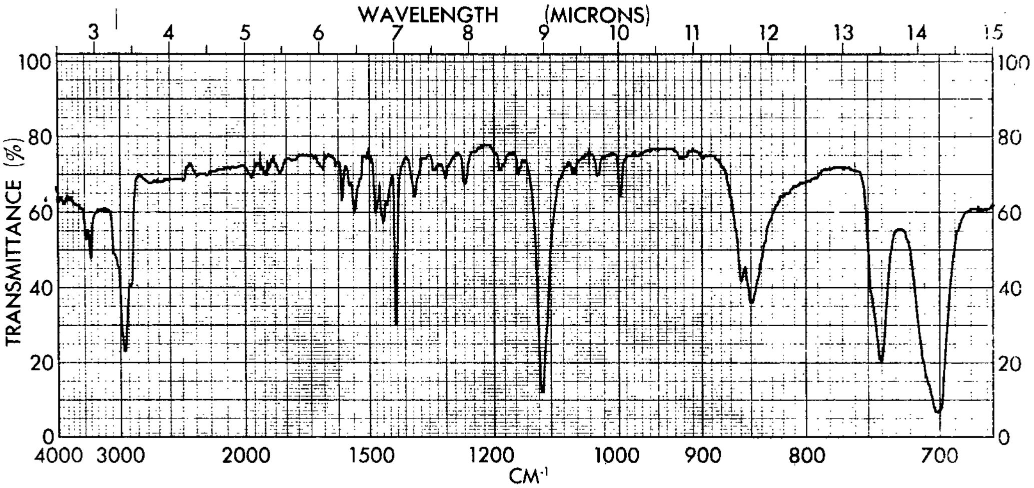

Figure 9 - Infrared Spectrum of Triphenylsilylamine (Nujol)

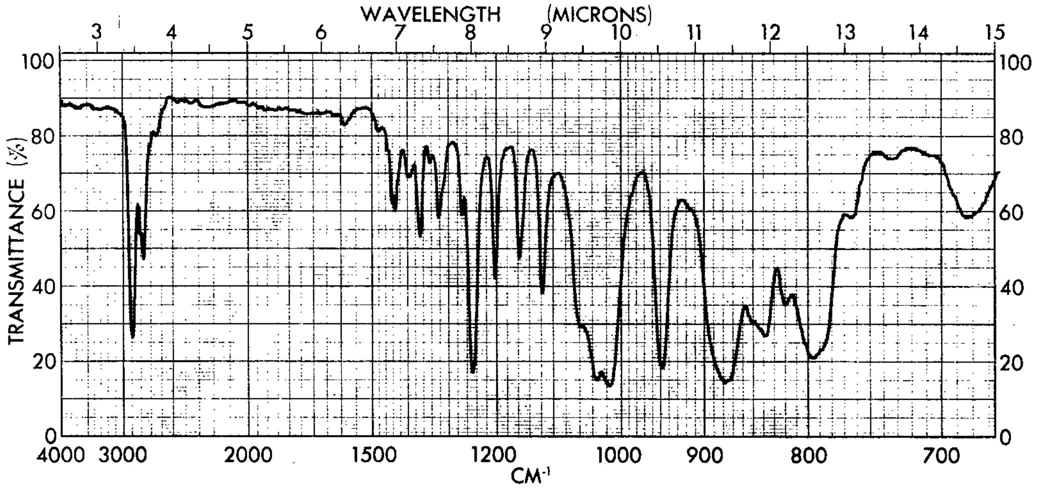

Figure 10 - Infrared Spectrum of N,N'-Bis[dimethyl(piperidino)silyl]-tetramethylcyclodisilazane (Liquid)

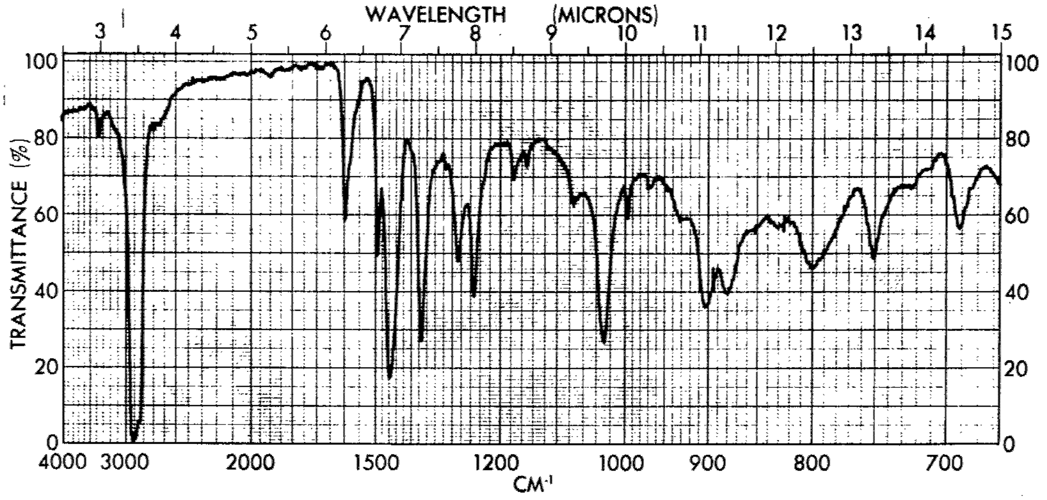

Figure 11 - Infrared Spectrum of N,N'-Bis(anilinodimethylsilyl)-tetramethylcyclodisilazane (Nujol)

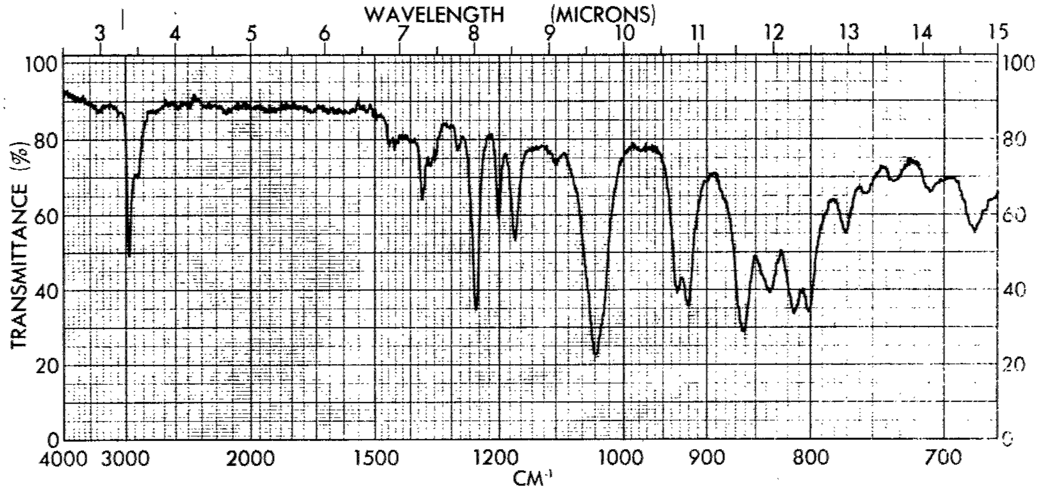

Figure 12 - Infrared Spectrum of the Product of Treating Bis-(chlorodimethylsilyl)trimethylsilylamine with the Lithium Salt of Diethylamine (Liquid)

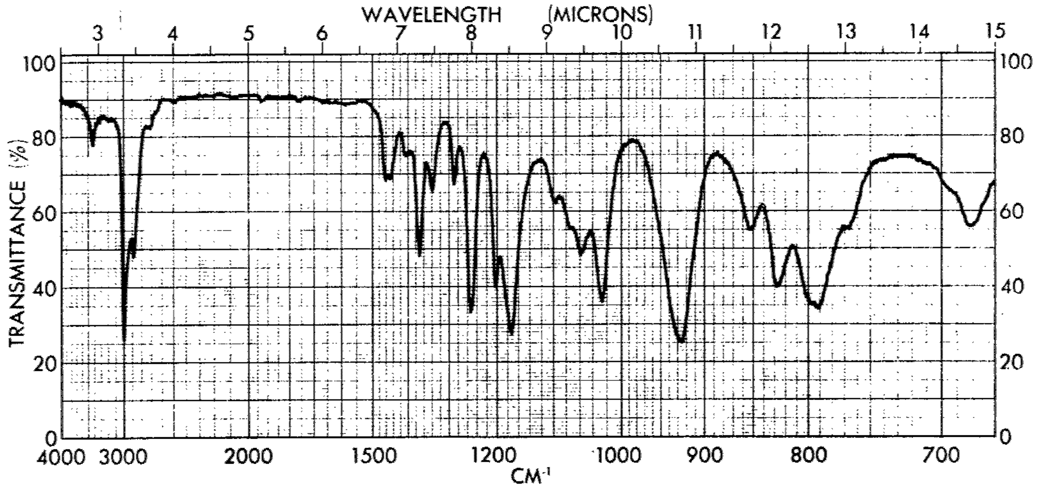

Figure 13 - Infrared Spectrum of 1,3-Bis(diethylamino)-1,1,3,3-tetramethyldisilazane (Liquid)

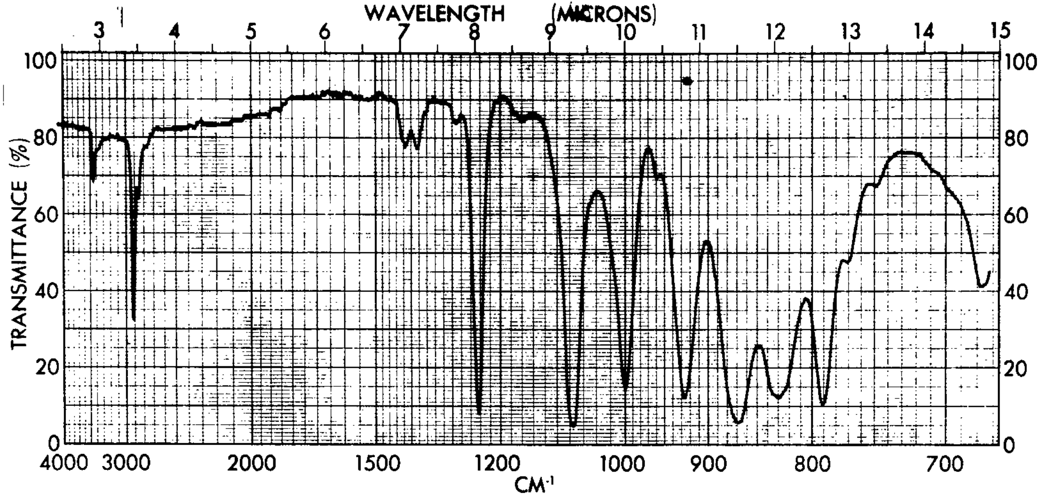

Figure 14 - Infrared Spectrum of 1-Trimethylsilyltetramethylcyclodisilazane (Liquid)

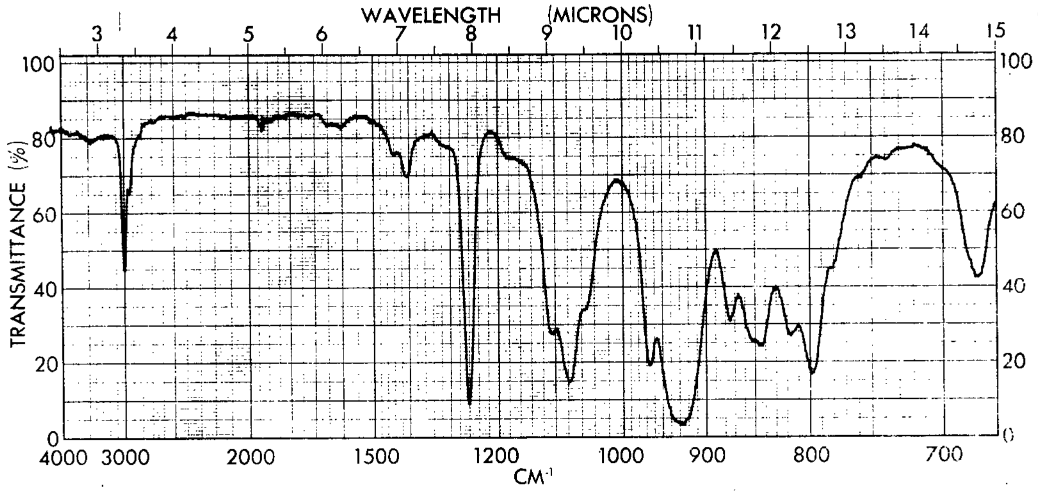

Figure 15 - Infrared Spectrum of 1,5-Bis(trimethylsilyl)-2,2,-4,4,6,6,8,8-octamethyl-1,5-diaza-3,7-dioxa-2,4,-6,8-tetrasilacyclooctane (Liquid)

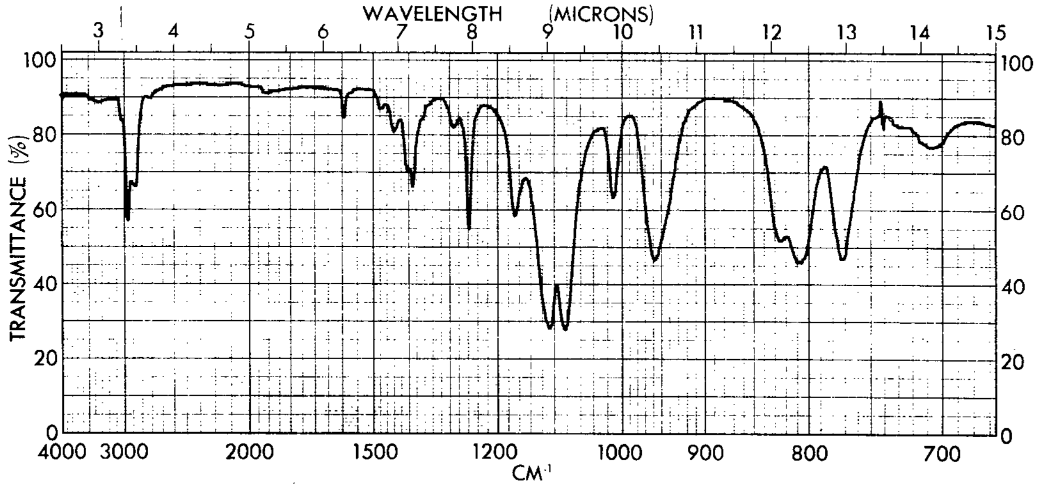

Figure 16 - Infrared Spectrum of Diethoxymethylvinylsilane (Liquid)

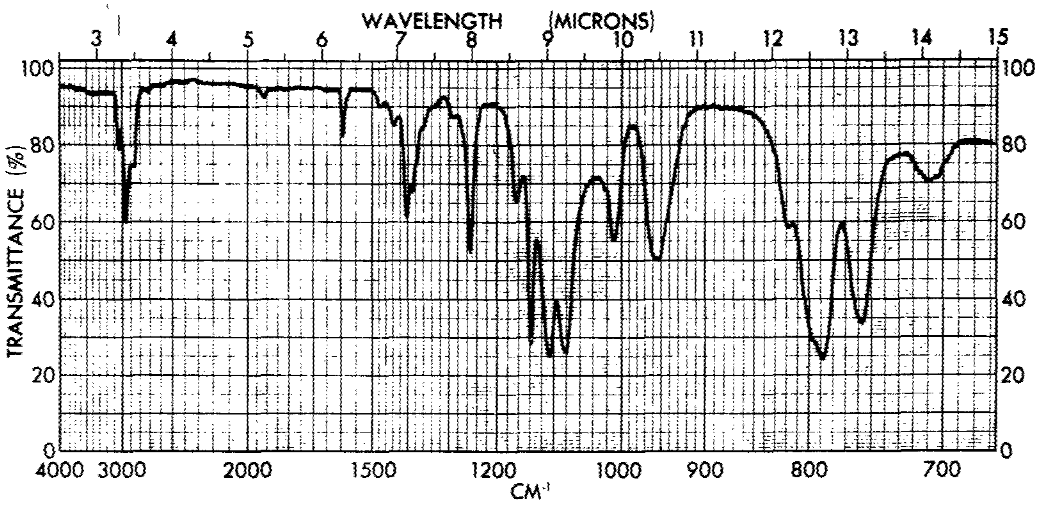

Figure 17 - Infrared Spectrum of p-Phenylenebis(ethoxymethylvinylsilane) (Liquid)

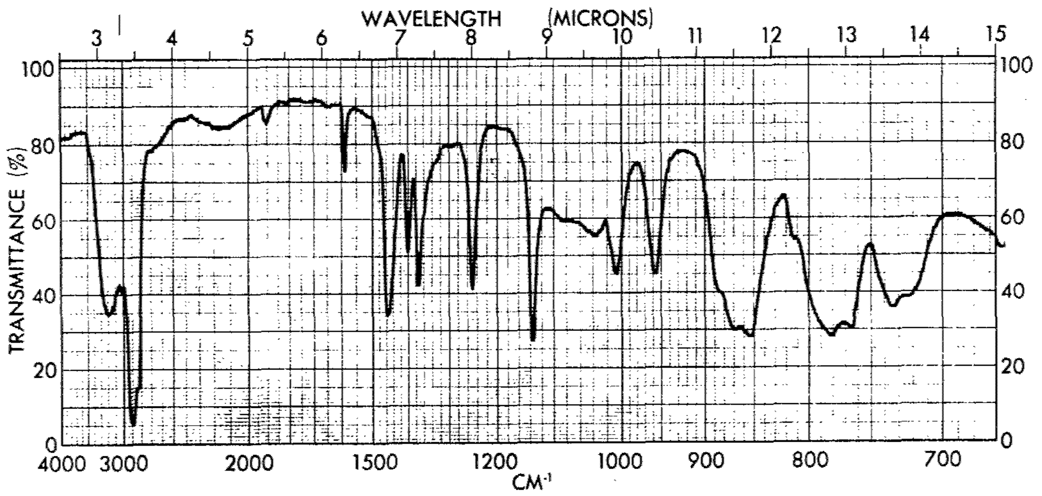

Figure 18 - Infrared Spectrum of p-Phenylenebis(hydroxymethylvinylsilane) (Nujol)

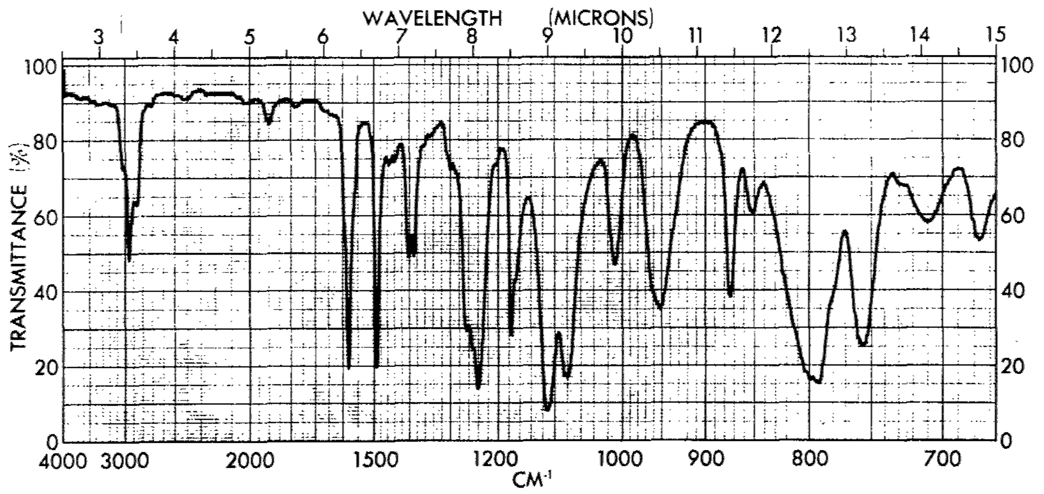

Figure 19 - Infrared Spectrum of Bis(p-ethoxymethylvinylsilylphenyl) Ether (Liquid)

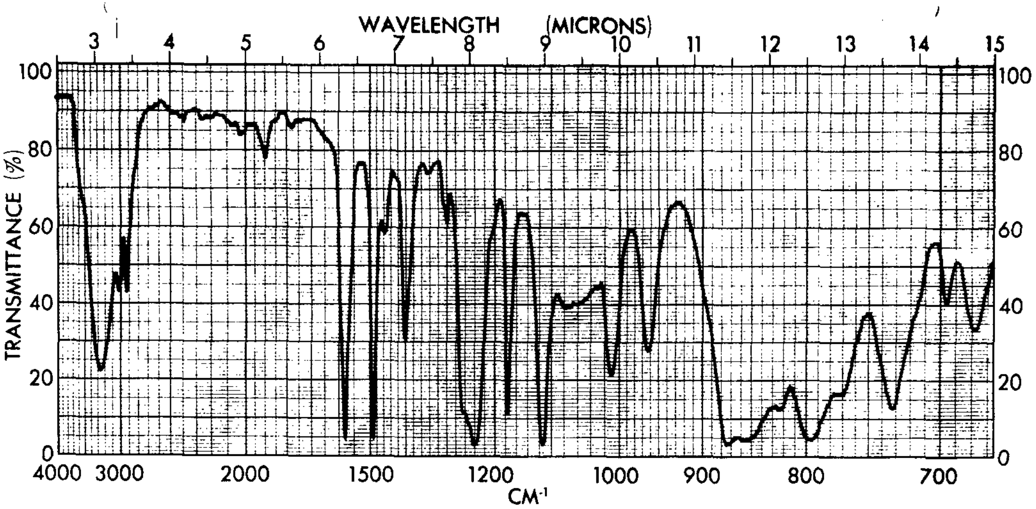

Figure 20 - Infrared Spectrum of Bis(p-hydroxydimethylsilylphenyl) Ether (Liquid)

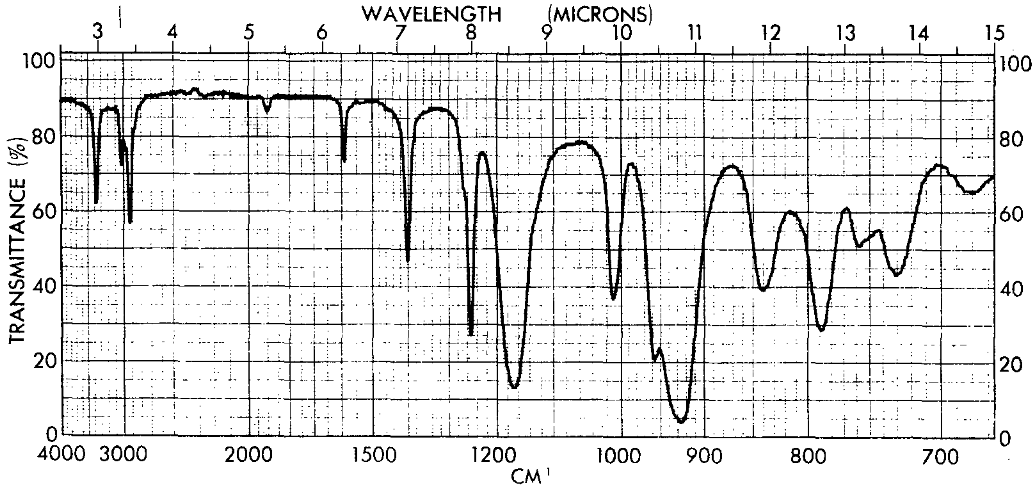

Figure 21 - Infrared Spectrum of 2,4,6-Trimethyl-2,4,6-trivinylcyclotrisilazane (Liquid)

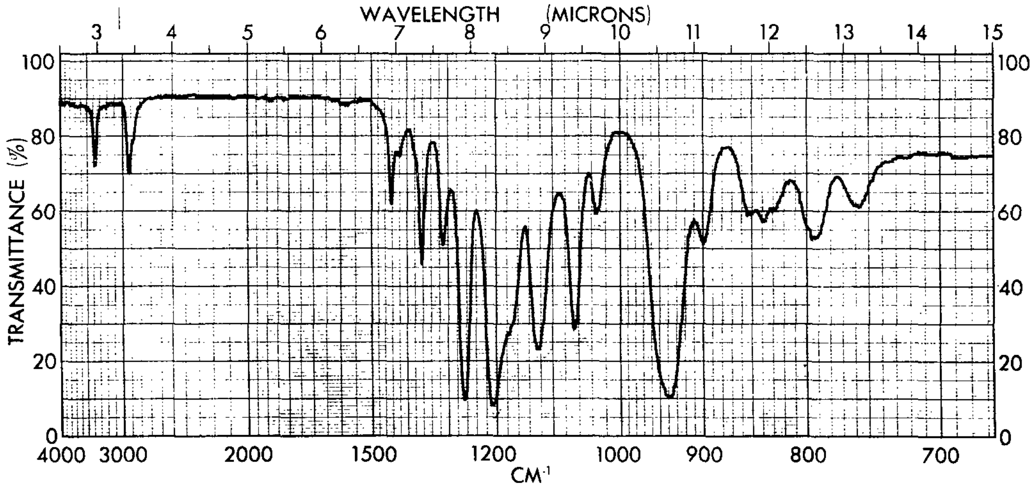

Figure 22 - Infrared Spectrum of 2,4,6-Trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane (Smear)

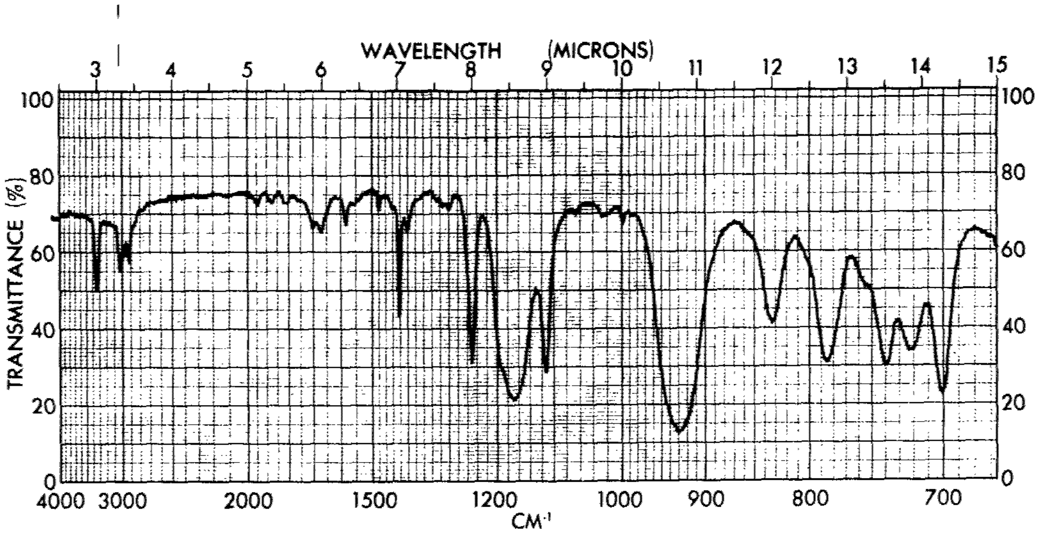

Figure 23 - Infrared Spectrum of 2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilazane (Smear)

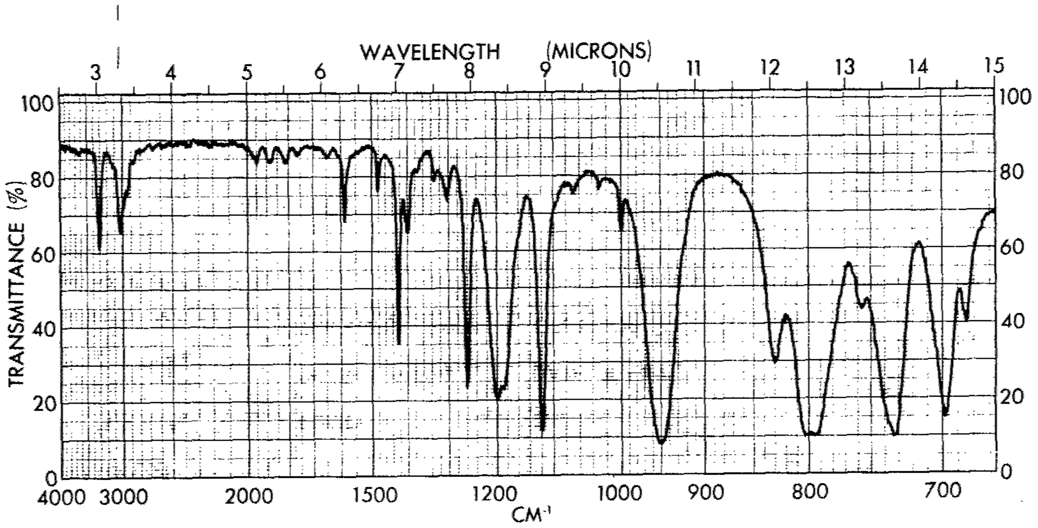

Figure 24 - Infrared Spectrum of 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisilazane (Liquid)

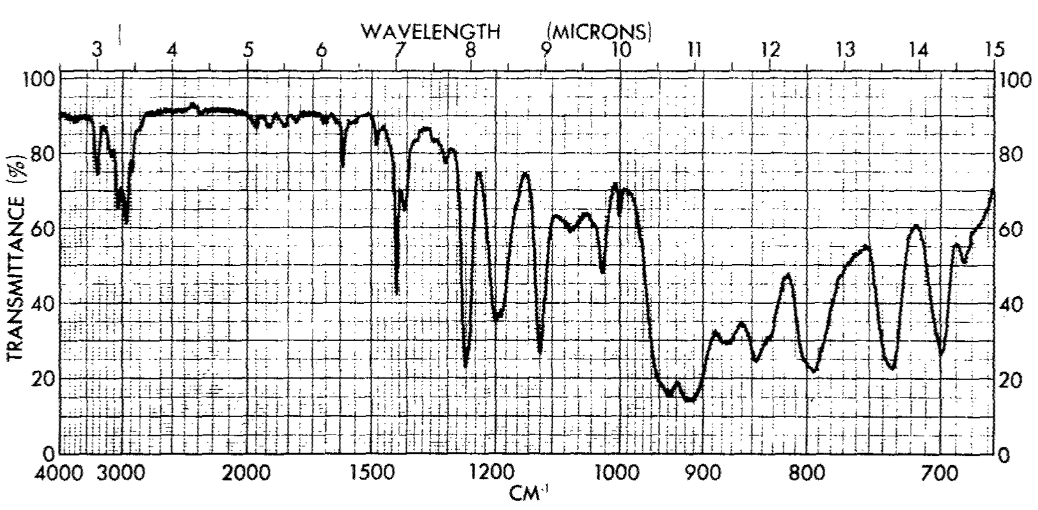

Figure 25 - Infrared Spectrum of the Product of Treating 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisilazane with Sodium Bis(trimethylsilyl)amide (Liquid)

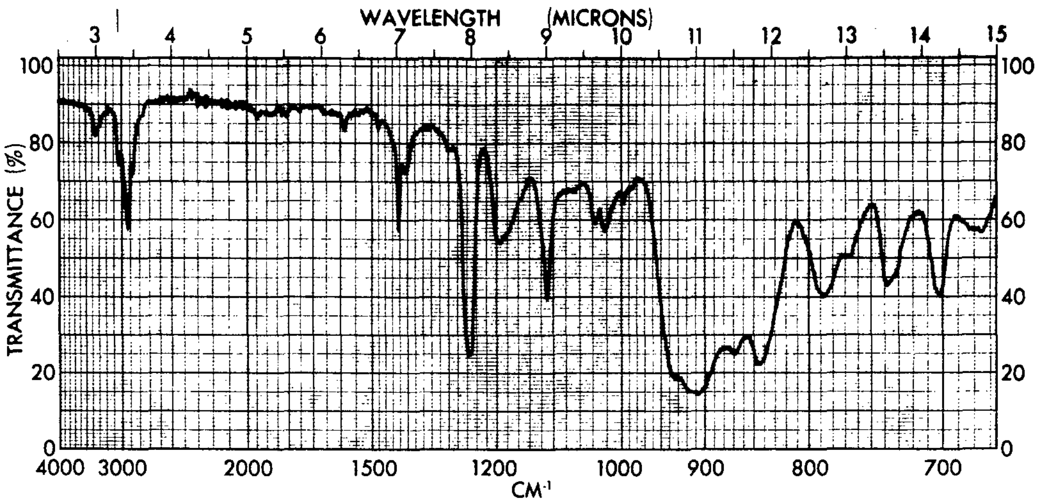

Figure 26 - Infrared Spectrum of the Product of Treating the Condensate from 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisilazane and Sodium Bis(trimethylsilyl)amide with Dimethylamine (Smear)

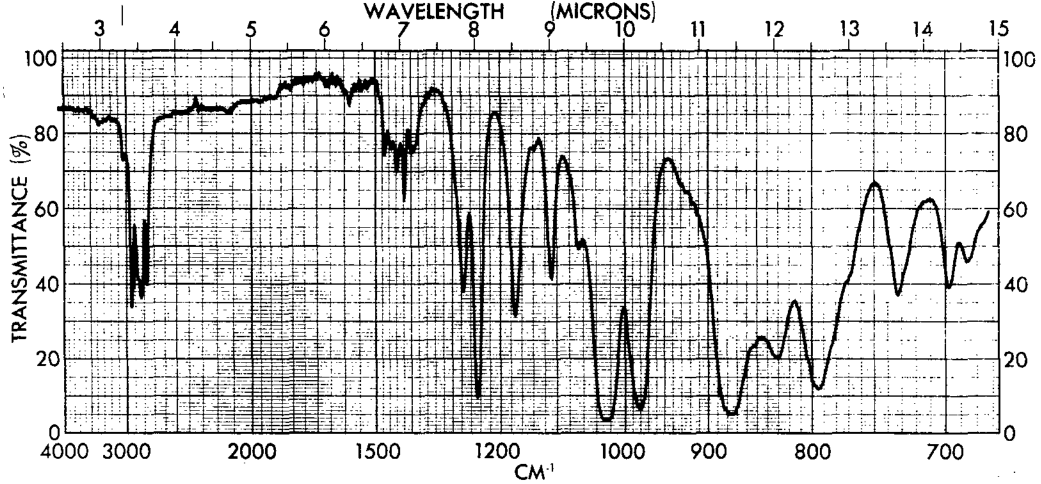

Figure 27 - Infrared Spectrum of the High Boiling Fraction from the Equilibration of N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane and Dichloromethylphenylsilane Quenched with Dimethylamine (Liquid)

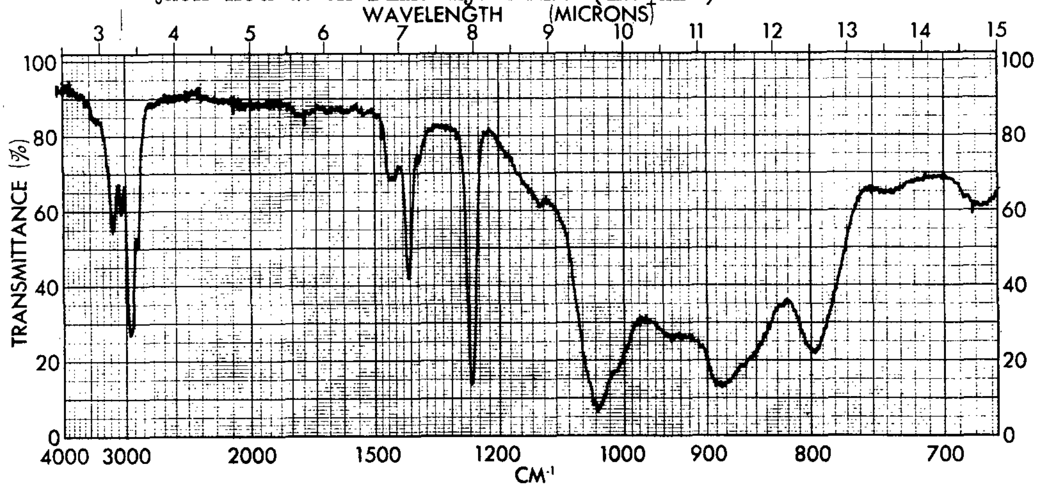

Figure 28 - Infrared Spectrum of the Nonvolatile Material Obtained by Heating N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane with Aluminum Chloride (Nujol)

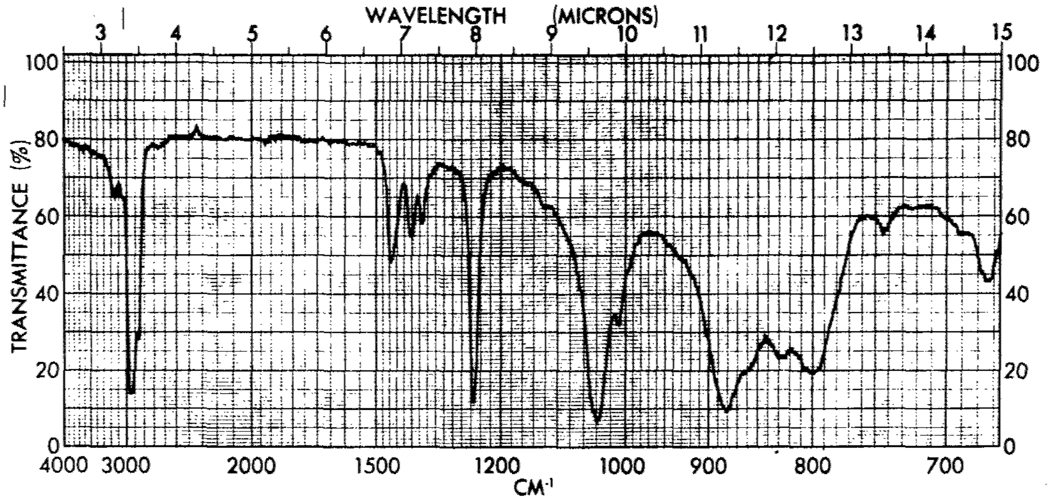

Figure 29 - Infrared Spectrum of a Solid Distillate Obtained After Heating N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane with Aluminum Chloride (Nujol)

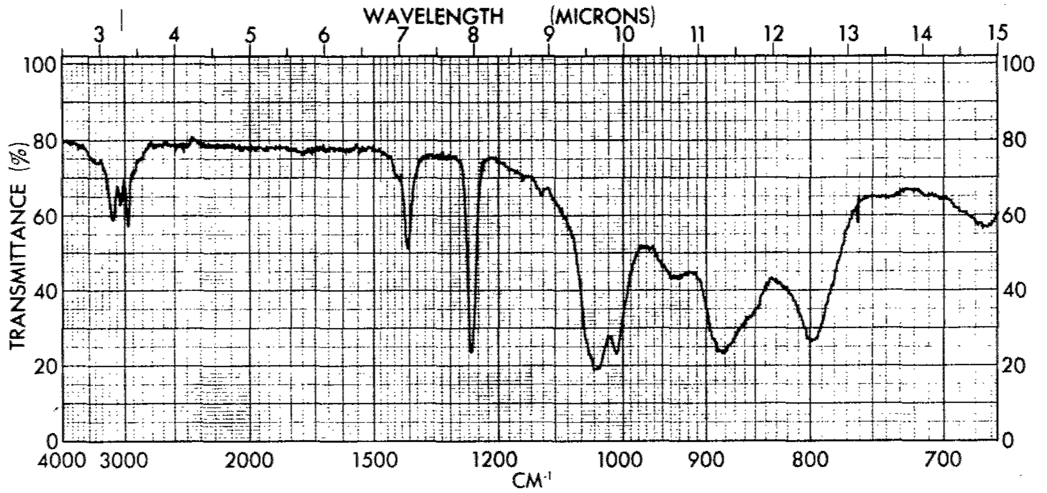

Figure 30 - Infrared Spectrum of a Liquid Distillate Obtained After Heating N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane with Aluminum Chloride (Liquid)

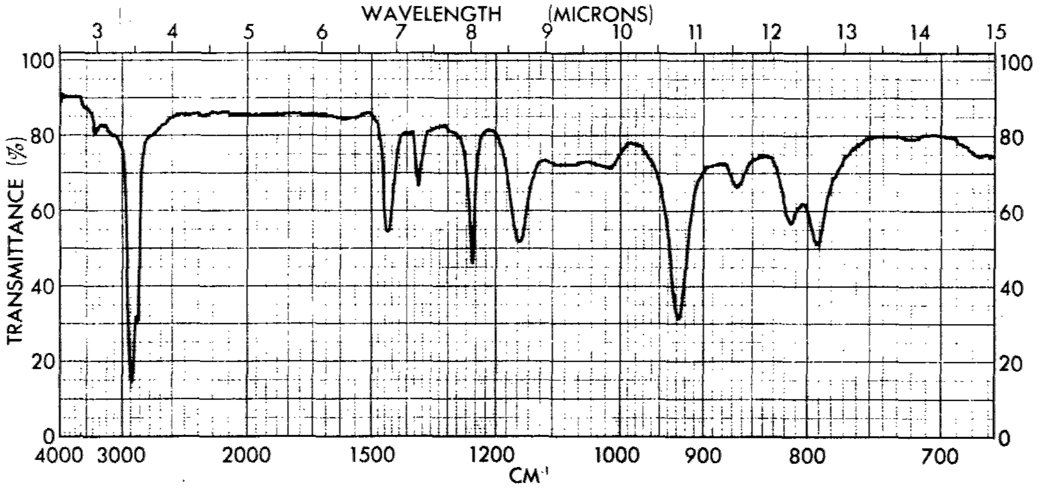

Figure 31 - Infrared Spectrum of the Product of Treating Hexamethylcyclotrisilazane with Sodium Amide (Nujol)

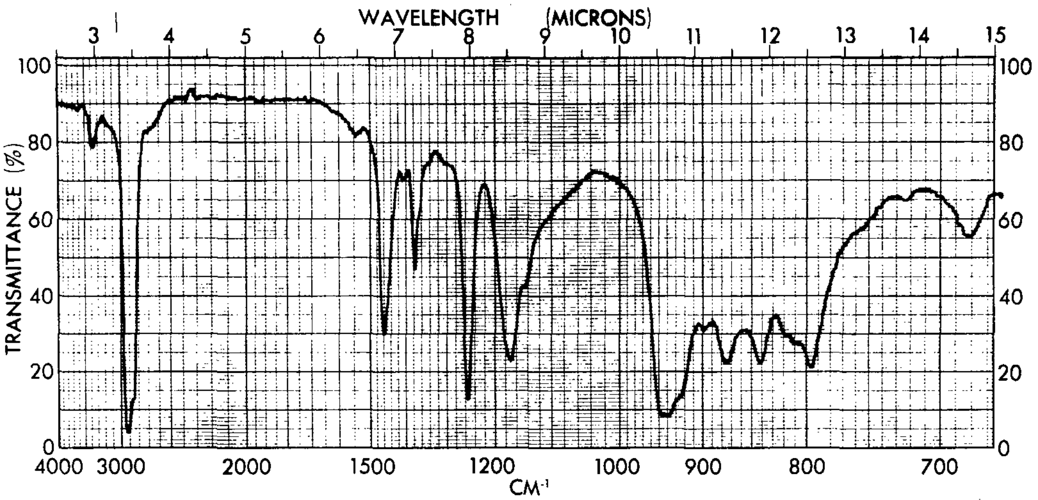

Figure 32 - Infrared Spectrum of the Product of Treating N-trimethylsilylhexamethylcyclotrisilazane with Sodium Amide (Nujol)

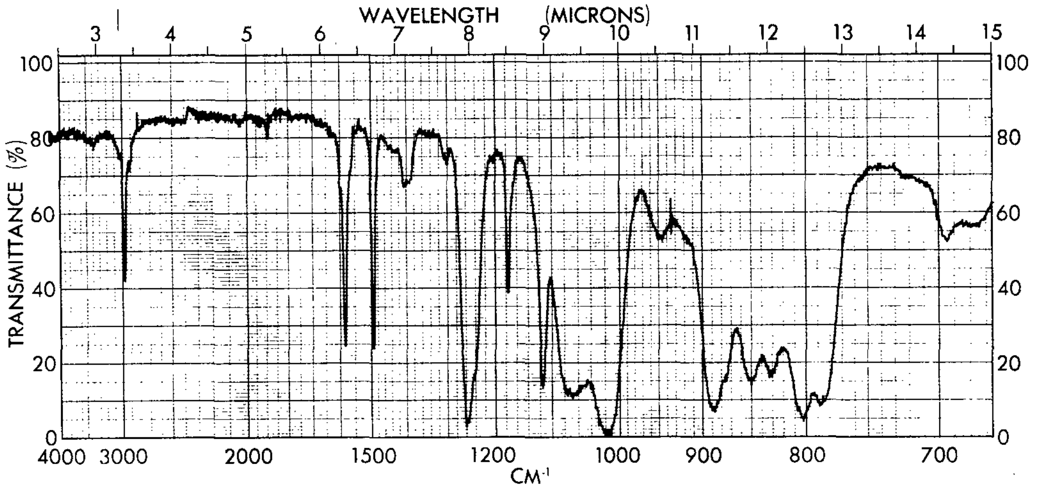

Figure 33 - Infrared Spectrum of a Polymer from Bis(p-hydroxydimethylsilylphenyl) Ether and N,N'-Bis[(dimethylamino)-dimethylsilyl]tetramethylcyclodisilazane Endcapped with Bis(trimethylsilyl)acetamide (Film)

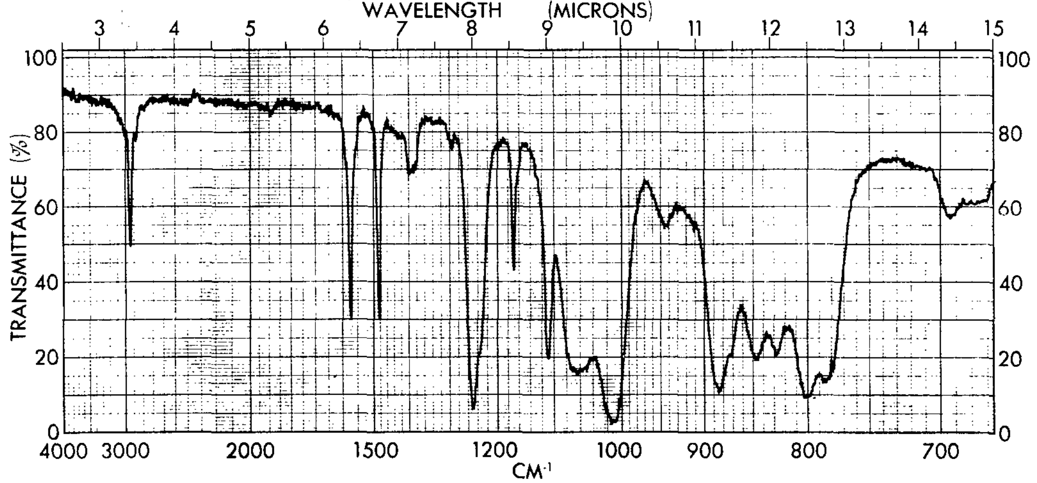

Figure 34 - Infrared Spectrum of the Polymer in Figure 33 After it was Washed with Water (Film)

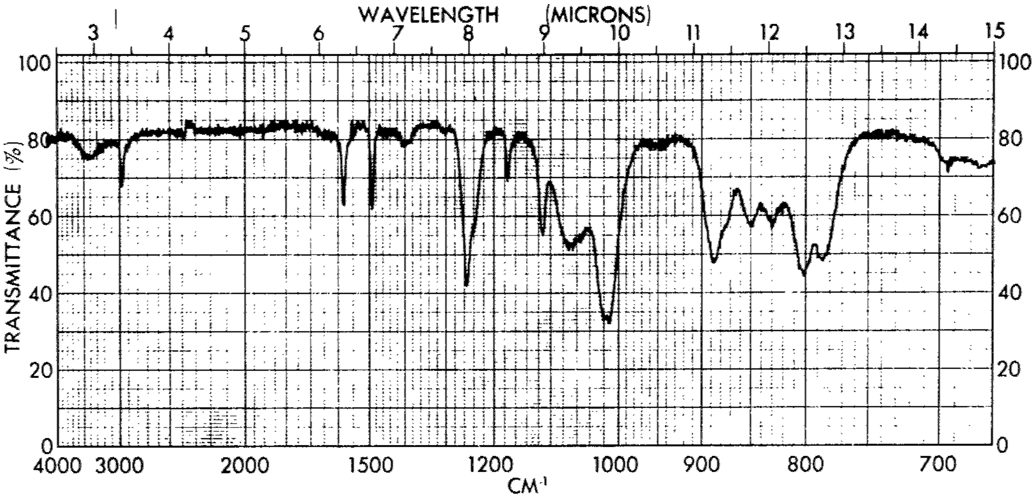

Figure 35 - Infrared Spectrum of a Polymer Sample from N,N'-Bis-[(dimethylamino)dimethylsilyl]tetramethylcyclodisilazane and Bis(p-dimethylhydroxysilyl)phenyl Ether, η_{inh} = 0.26 dl/g (film)

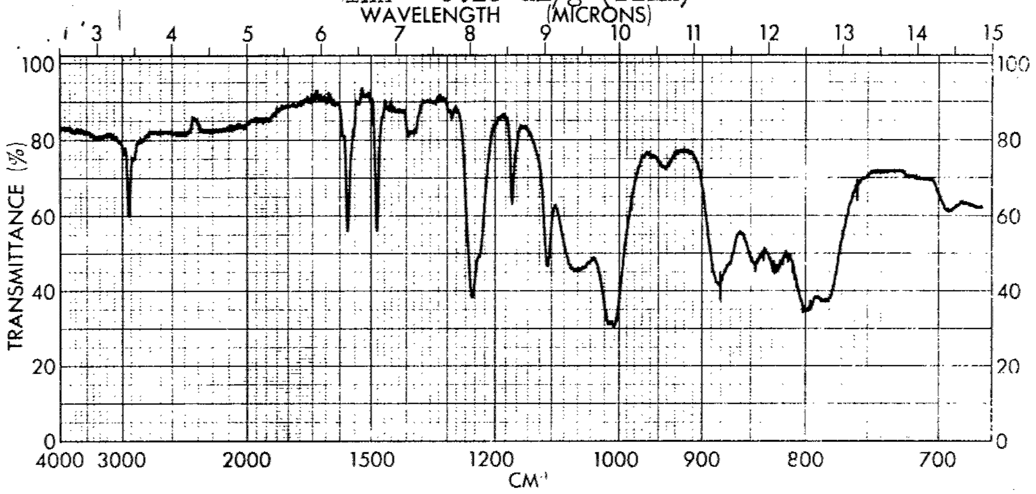

Figure 36 - Infrared Spectrum of a Polymer Sample from N,N'-Bis-[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and Bis(p-dimethylhydroxysilyl)phenyl Ether, η_{inh} = 0.80 dl/g (Film)

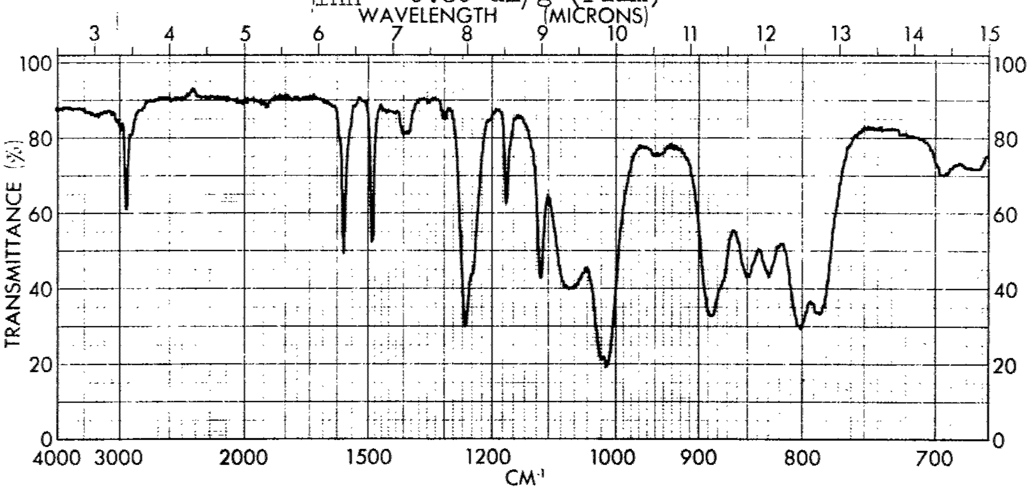

Figure 37 - Infrared Spectrum of a Polymer Sample from N,N'-Bis-[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and Bis(p-hydroxydimethylsilylphenyl) Ether, η_{inh} = 0.89 dl/g (Film)

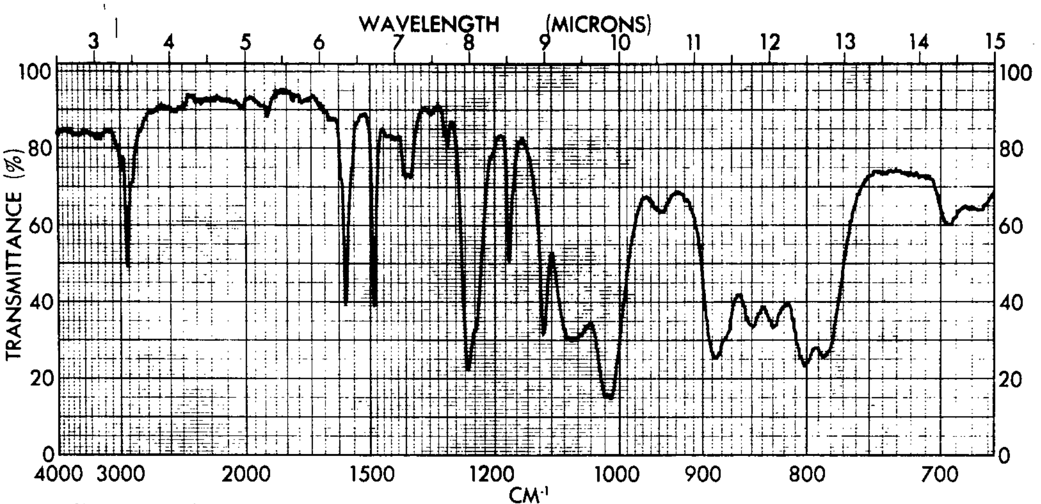

Figure 38 - Infrared Spectrum of a Crosslinked Polymer Sample from N,N'-Bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and Bis(p-hydroxydimethylsilylphenyl Ether (Film)

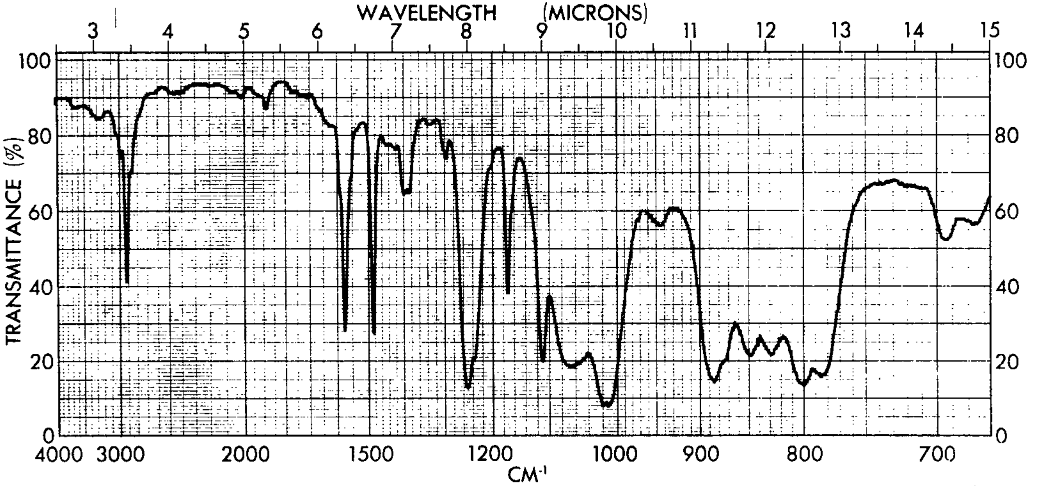

Figure 39 - Infrared Spectrum of a Second Crosslinked Polymer Sample from N,N'-Bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and Bis(p-hydroxydimethylsilylphenyl) Ether (Film)

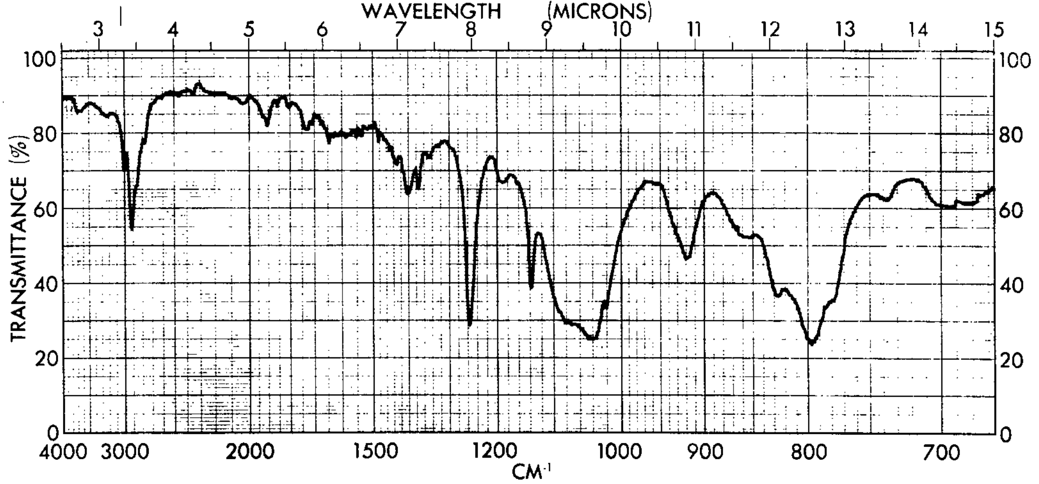

Figure 40 - Infrared Spectrum of a Polymer from Decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane, p-Phenylenebis-(dimethylsilanol), and p-Phenylenebis(methylvinylsilanol), η_{inh} = 0.72 dl/g (Film)

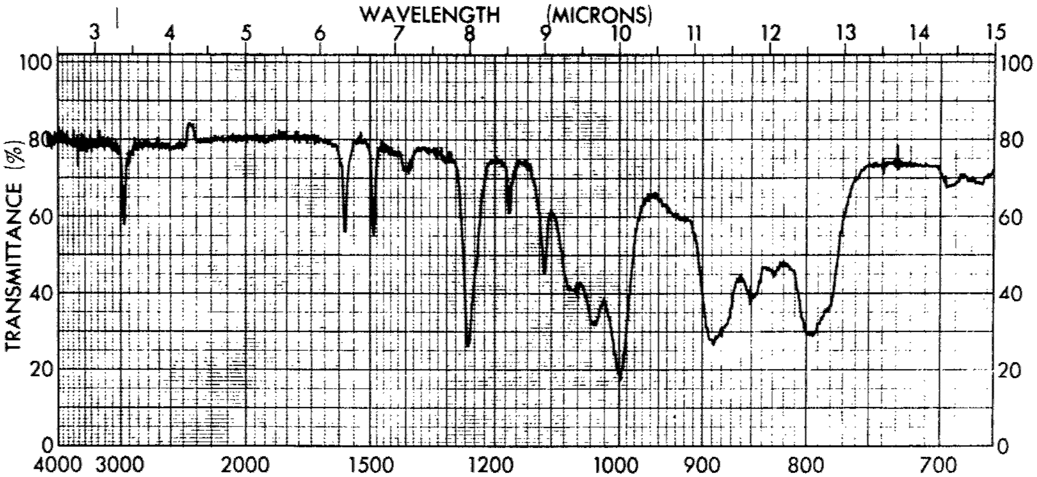

Figure 41 - Infrared Spectrum of a Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and the Dimethylamino Derivative of the Oligocyclodisilazane with Two Rings (Film)

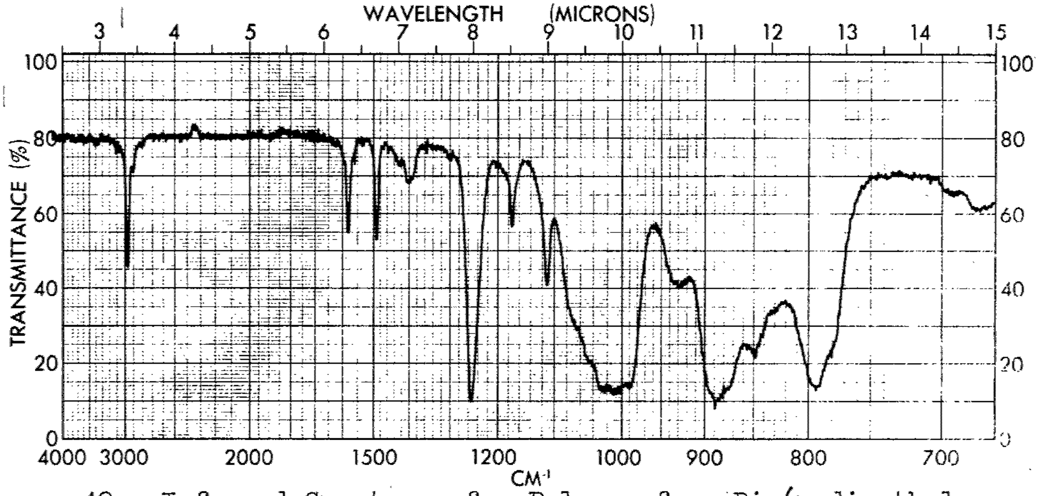

Figure 42 - Infrared Spectrum of a Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and the Dimethylamino Derivative of the Oligocyclodisilazane with Four Rings (Film)

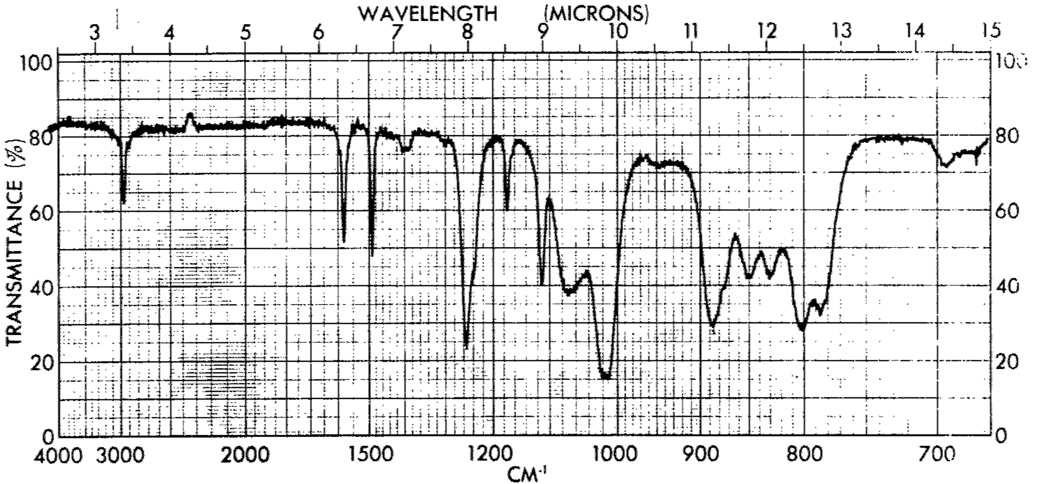

Figure 43 - Infrared Spectrum of a Polymer from Bis(p-dimethylhydroxysilylphenyl) Ether and N,N'-Bis[(dimethylamino)-dimethylsilyl]tetramethylcyclodisilazane that was Used in the Study of its Hydrolytic Stability (Film)

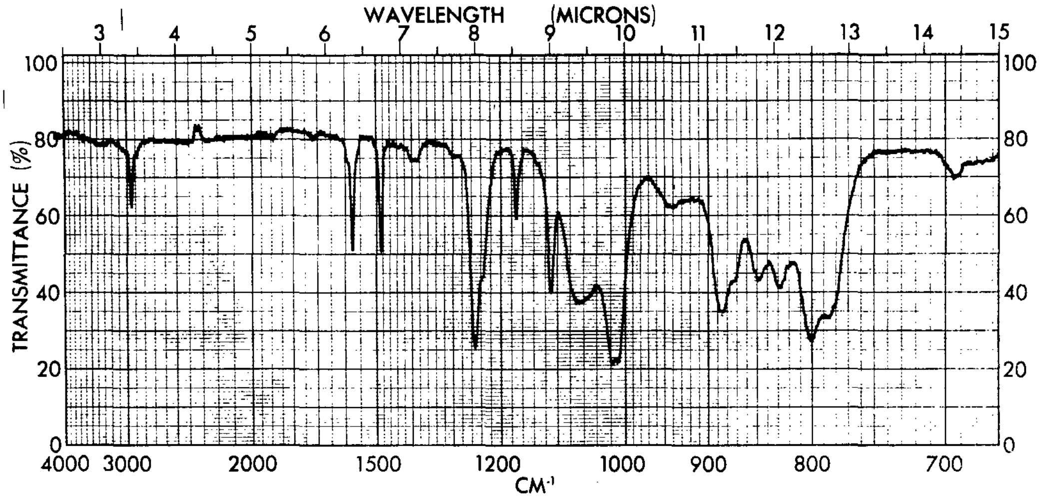

Figure 44 - Infrared Spectrum of the Polymer in Figure 15 After Being Exposed to Moist Air for 22 Hr. (Film)

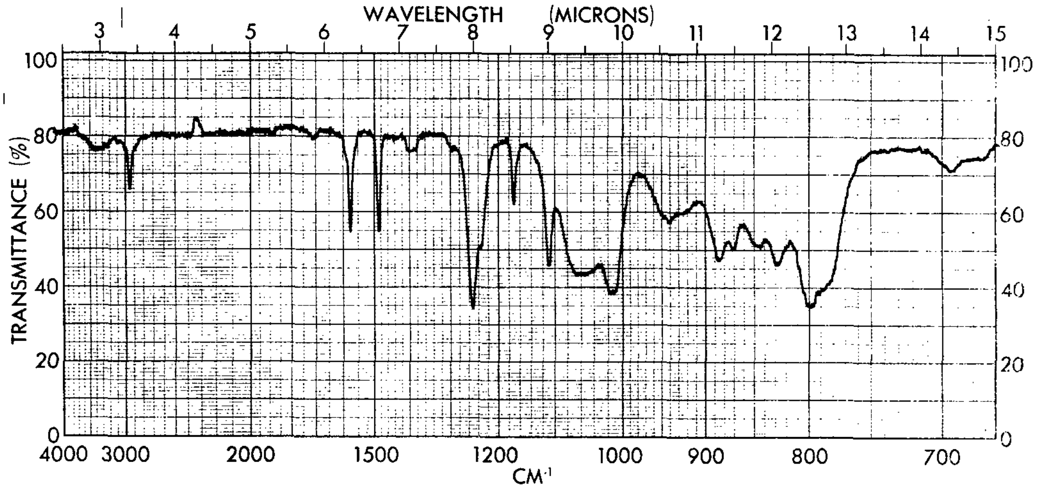

Figure 45 - Infrared Spectrum of the Polymer in Figure 15 After Being Exposed to Moist Air for 48 Hr. (Film)

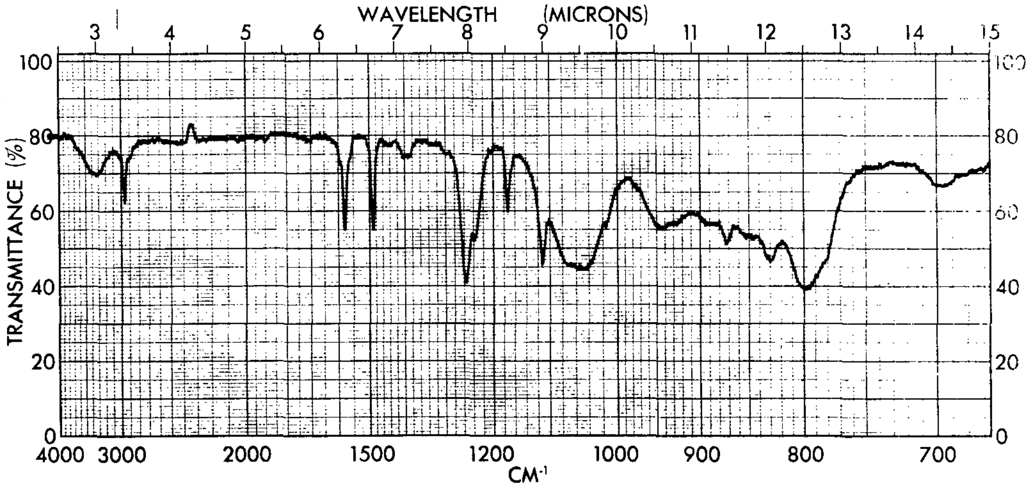

Figure 46 - Infrared Spectrum of the Polymer in Figure 15 After Being Exposed to Moist Air for 66 Hr. (Film)

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11. SUPPLEMENTARY NOTES

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13. ABSTRACT

In condensation polymerizations of N,N'-bis[(dialkylamino)dimethylsilyl]tetramethylcyclodisilazane and bis(p-hydroxydimethylsilylphenyl) ether, storage-stable, toluene-soluble polymers can be obtained provided the compositions are suitably stabilized with bis(trimethylsilyl)acetamide. If the dimethylamino derivative of the cyclodisilazane is used in the polymerization, polymers with inherent viscosities of about 0.3 dl/g are obtained; if the diethylamino derivative is used, polymers with inherent viscosities as high as 0.9 dl/g are produced. Other monomers examined in a preliminary way include the piperidino derivative of the cyclodisilazane and p-phenylenebis(methylvinylsilanol). Synthesis procedures are reported for p-phenylenebis(methylvinylsilanol), bis(p-hydroxydimethylsilylphenyl) ether, N,N'-bis[dimethyl(piperidino)silyl]tetramethylcyclodisilazane, 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane, 2,4,6-trimethyl-2,4,6-tris(-3,3,3-trifluoropropyl)cyclotrisilazane, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane, and various other intermediates and monomers. Several approaches are described for the preparation of phenyl-substituted cyclodisilazane monomers, and some additional investigations of equilibrium redistribution reactions are reported.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Polymers						
Synthetic Methods						
Silicon-Nitrogen Compounds						